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EVALUATE AND CHARACTERIZE MECHANISMS CONTROLLING TRANSPORT, FATE, AND EFFECTS OF ARMY SMOKES IN THE AEROSOL WIND TUNNEL

Transport, Transformations, Fate, and Terrestrial Ecological Effects of Hexachloroethane Obscurant Smokes

Final Report

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The terrestrial transport, chemical fate, and ecological effects of hexachloroethane (HC) smoke were evaluated under controlled wind tunnel conditions. The primary objectives of this research program are to characterize and assess the impacts of smoke and obscurants on: 1) natural vegetation characteristic of U.S. Army training sites in the United States; 2) physical and chemical properties of soils representative of these training sites; and 3) soil microbiological and invertebrate communities. Impacts and dose/responses were evaluated based on exposure scenarios, including exposure duration, exposure rate, and sequential cumulative dosing. Key to understanding the environmental impacts of HC smoke/obscurants is establishing the importance of environmental parameters such as relative humidity and wind speed on airborne aerosol characteristics and deposition to receptor surfaces. Direct and indirect biotic effects were evaluated using five plant species and two soil types.

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HC aerosols were generated in a controlled atmosphere wind tunnel by combustion of hexachloroethane mixtures prepared to simulate normal pot burn rates and conditions. The aerosol was characterized and used to expose plant, soil, and other test systems. Particle sizes of airborne HC ranged from 1.3 to 2.1 μm mass median aerodynamic diameter (MMAD), and particle size was affected by relative humidity over a range of 20% to 85%. Air concentrations employed ranged from 130 to 680 mg/m^3, depending on exposure scenario. Chlorocarbon concentrations within smokes, deposition rates for plant and soil surfaces, and persistence were determined. The fate of principal inorganic species (Zn, Al, and Cl) in a range of soils was assessed.

Based on a deposited foliar dose (mass loading) of 12 to 40 μg HC/cm^2, equivalent to 1- to 4-h exposure to smokes at 450 mg/m^3 air, plant toxicity responses are judged low to moderate. Relative humidity has no dramatic effect on the quality or intensity of damage. Repetitive dosing at 2- to 3-day intervals resulted in substantially more damage than indicated by the total delivered dose. The observed effects likely result from the accumulation of Zn from foliar surfaces and subsequent toxicity. Residual effects, namely those that result from foliar absorption of smoke constituents that are transferred to below ground plant tissues, are apparent, although not severe in several of the test series. Indirect plant effects resulting from the growth of plants on HC-contaminated soils indicated no significant effects of HC on grass growth through two or three harvests. In no case was seed germination affected.

Soil microbial activities were affected by HC aerosols deposited to soils. Soil microbial respiration was depressed for up to 15 days, as were dehydrogenase and phosphatase activities. Decreases in nitrifying bacteria populations were also observed. Effects of HC smokes were more pronounced for sandy soils than in more fertile soils. Earthworm bioassays indicated no adverse effect of HC smokes on survival, at soil doses of 8 μg Zn/cm^2 or 32 μg HC/cm^2.

EXECUTIVE SUMMARY

Effective training scenarios for our armed forces require that troop maneuvers simulate, as closely as possible, the conditions most likely to be encountered under live combat situations (e.g., hardware, weapons fire, terrain, weather, vegetation, and smoke concentrations). Within the framework of the training operations, the U.S. Army has a regulatory responsibility to ensure that the use of smokes and obscurants does not adversely affect the health of local residents or the environment, both on and near the training sites. The environments of these training centers range from high deserts to semitropical forests, thus complicating this responsibility. The Health Effects Research Division of the U.S. Army Biomedical Research and Development Laboratory (USABRDL) has been assigned the responsibility of determining the potential environmental effects associated with the use of smokes and obscurants in training and testing.

As part of USABRDL's planned program in response to this concern, this project was implemented to evaluate the formation, transport, chemical transformations, deposition, and the terrestrial ecological effects of smokes and obscurants currently used in training throughout the United States. Research related to smoke and obscurant testing employed a special recirculating wind tunnel that ensures containment of the smoke and permits simulation of a variety of environmental conditions (i.e., varying wind speeds, relative humidities, temperatures, and lighting conditions). The research described in this report addresses the environmental effects and fate of hexachloroethane (HC) smokes, and is similar to that performed with red phosphorus-butyl rubber and white phosphorus smokes (Van Voris et al. 1987) and for oil (Cataldo et al. 1989).

Within the framework of the experimental design, our first objective was to evaluate the influence of two primary environmental variables, relative humidity (20%, 60%, 90%, and simulated rain) and wind speed (0.90 to 4.5 m/s, or 2 to 10 mph), on the ecological effects of HC smokes. Our second objective was to characterize the physical and chemical properties of HC Smokes. USABRDL will use this information in predicting dose associated with human risk assessment models and for future assessments of smoke and obscurants effects on wildlife and domestic animals.

Environmental wind tunnels provide a method for the dynamic exposure of environmental components, such as plants and soils, and subsequent elucidation of the fate and effects of obscurant smokes. This approach allows for the simulation of a

number of environmental variables affecting the physical and chemical nature of smoke aerosols. In the present studies, HC smokes were generated in scaled-down combustion pots to simulate normal burn conditions of temperature and oxygen, and introduced into the air stream of the recirculating tunnel, remote from the test section, to simulate aged aerosols that would be deposited 1500 m from the generator. Several environmental parameters were investigated, including exposure duration, relative humidity, wind speed, rainout during exposure, and post-exposure simulated rainfall. Aerosols were continually monitored for concentration and size distribution to permit intercomparisons from test to test.

Several plant species and soil types were investigated based on dose response, intensity, and recovery. Plants were selected to be representative of native species found at regional training facilities. Investigations centered on elucidation of those physical parameters and processes affecting environmental performance resulting from recurrent use of obscurant smokes. Environmental components evaluated included foliar contact toxicity, indirect effects of soil contamination on plant growth, effects of soil-deposited smoke on soil microbial enzyme activity, and effects on earthworms. In all cases, responses were correlated with delivered dose/mass loading and not airborne smoke concentration.

The results for HC smokes indicate a low to moderate impact to plants following direct foliar deposition, and little residual effects. Indirect soil/plant effects were minimal in most instances, and are not to be expected to be persistent. Overall, damage intensity was lower than observed for phosphorus smokes, but more than for fog oil. Soil microbial processes important in mineral cycling were affected. No adverse effects were noted in the earthworm assays.

These studies were designed to enable prediction of environmental damage under a variety of field conditions. The versatility of these data to meet this use relies on measurements of dose/response relationships based on mass loading, and characterization of aerosol parameters allowing calculation of deposition velocities for specific receptor surfaces under specific environmental variables. For example, the length of time that a smoke test could be conducted without adversely affecting a specific plant species located 8 km downwind could easily be calculated based on the air concentration at that point, the deposition velocity for that canopy type, and wind speed. It is this predictive approach based on precise laboratory or field data that will be most useful in the future.

FOREWARD

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1.0 INTRODUCTION

The U.S. Army has deployed a number of smokes and obscurants to mask visually the movement of troops and vehicles during combat. Effective training scenarios for our armed forces require that troop maneuvers simulate, as closely as possible, the conditions most likely to be encountered under live combat situations (e.g., hardware, weapons fire, terrain, weather, vegetation, and smoke concentrations). Within the framework of the training operations, the Army has a regulatory responsibility to ensure that the use of smokes and obscurants does not adversely affect the health of local residents, or the environment, both on and near the training sites. The environments of these training centers range from high deserts to semitropical forests, thus complicating this responsibility.

The Health Effects Research Division of the U.S. Army Biomedical Research and Development Laboratory (USABRDL) has been assigned the responsibility of determining the potential environmental effects associated with the use of smokes and obscurants in training and testing. As part of USABRDL's planned program in response to this concern, the present study was designed to evaluate the transport, the chemical transformation, and the terrestrial ecological effects of several of the smokes currently used in training throughout the United States. The present study expands on prior field studies in two major aspects. First, smoke and obscurant testing is conducted within a special recirculating wind tunnel that ensures containment of the smoke and allows simulation of a variety of environmental conditions (i.e., varying wind speeds, relative humidities, temperatures and lighting conditions), under dynamic exposure conditions. Second, the complex chemical nature of obscurant smokes, such as HC (hexachloroethane), requires that chemical transformations be correlated with environmental effects.

Within the framework of the experimental design, the primary objective was to assess the influence of two primary environmental variables, relative humidity (20%, 60%, 90%, and simulated rain) and wind speed (2 to 10 mph or 0.90 to 4.5 m/s), on the ecological effects induced by smokes. The second overall objective was to characterize the physical and chemical properties of smokes for use by USABRDL in predicting dose associated with human health risk assessment models and for future assessments with regard to effects on wildlife and domestic animals.

It should be noted that the health and environmental effects of Army smokes and obscurants have been studied intensively over the past 30 years; these research efforts have recently been compiled and reviewed by Shinn et al. (1985). In general, research into the effects of obscurant smokes has concentrated on animal and aquatic toxicity, with relatively

little effort being expended in understanding soil/plant or ecological effects. The vast majority of these previous efforts used direct artificial dosing of organisms or aqueous amendments of suspected toxicants. While this may be appropriate and necessary in many instances, it may not be appropriate in developing an understanding of the potential impact of the recurrent use of obscurant smokes at heavily used training sites. This is mainly because there is no established correlation between airborne smoke concentration, deposition on soils and plants (duration and physical parameters affecting deposition), and the ultimate effect, environmental deterioration.

Environmental Behavior of HC Smokes. Hexachloroethane (HC) smokes are generated from a pyrotechnic mixture containing principally Al, ZnO, and C_2Cl_6 (hexachloroethane). Combustion of this mixture produces smokes containing Al_2O_3, $ZnCl_2$, and several organic species. The primary organic products are carbon tetrachloride (CCl_4), tetrachloroethane (C_2Cl_4), hexachlorobenzene (C_6Cl_6), unreacted hexachloroethane (C_2Cl_6), and possibly phosgene (Cichowicz 1983; Katz et al. 1980).

Much of the research on the toxicity and effects of hexachloroethane (HC) smokes has been limited to animal and aquatic studies (reviewed by Cichowicz 1983). The majority of these efforts have concentrated on the major inorganic components (Zn, Al), the organic component hexachloroethane, and the reaction by-products, namely phosgene, carbon tetrachloride, and hexachlorobenzene. Little or no research has been done with respect to soil/plant effects and fate, with the exception of Zn toxicity. With this limitation, and keeping in mind some of the previous discussion, it becomes clear that a detailed understanding of ecological effects of HC smokes is needed. In addition, the combustion of hexachloroethane, depending on burn configuration and aerosol age, will influence the chemical composition of aerosols, and thus the potential ecological impacts of its use. Both aspects need to be addressed. Questions which will be considered include: 1) dose/effect relationships for HC resulting from direct contact and indirect effects from soil contamination; 2) effects of HC deposited to soils, and its effect on nutrient availability and acid effects on contaminant solubilization; and 3) the effect of HC on microbial nitrification and community survival in soils.

Soil/Plant Interactions. Previous research efforts with red phosphorus/butyl rubber (RP/BR) and white phosphorus (WP) smokes (Van Voris et al. 1987), and fog oil obscurants (Cataldo et al. 1988) attempted to simulate the interaction of obscurant smokes with vegetative surfaces and soils. The purpose of these prior efforts, and those for HC, is to determine whether or not the recurrent use of obscurant smokes at intensively used field sites can irreversibly alter the physical and biological characteristics of these training sites. The approach employed uses a wind tunnel to develop a smoke field, allows for a controlled

exposure of both soils and plants, and permits simulation of any number of factors affecting smoke characteristics. These include burn/vaporization conditions, smoke age, particle size and concentration, the presence and concentrations of organic chemical constituents, and relative humidity, temperature, windspeed, and turbulence.

In the area of plant effects, we will evaluate both direct and indirect impacts of HC obscurant smokes. To date, the direct effects have been limited to rather qualitative estimates of phenotypic foliar damage in perennial tree and shrub species, and dry matter production in fast growing perennial grass species. The indirect effects have been limited to regrowth of contaminated grasses, dry matter production of grasses grown on contaminated soils, and mobilization and plant uptake of inorganic elements from contaminated soils. This approach has been suitable to describe the influence of a range of treatment and environmental variables on the toxicity of smokes. However, much of this type of data is nonparametric in nature and not amenable to developing statistical response trends. In the present study, in addition to these nonparametric indicators, we also employ whole plant photosynthetic and respiratory response measurements to assess potential plant damage.

Much of the phytotoxicity observed with the phosphorus smokes appears to have resulted from either foliar acidity and/or salt effects, which are known to cause membrane and/or cellular disruption, followed by dieback of leaves and needles. This produces the range of phenotypic symptomatology reported for the phosphorus smokes such as foliar necrosis, tip dieback, and leaf drop. However, the residual effects observed in grass regrowth following foliar contamination and grass growth data from contaminated soils cannot be readily explained on this basis. It is suggested that these residual effects are caused by some constituent of the phosphorus smoke which is persistent in contaminated soils and available for plant uptake, plants, and in the case of foliar contamination, is readily absorbed through the foliage, and transported to the root where it exerts its residual effects. In comparison, the fog oil obscurants were substantially less damaging to terrestrial biota. The HC smokes, based on their known combustion products, required characterization of foliar and soil-deposited components to evaluate potential impacts.

On the whole, little definitive work has been done with respect to the ecological effects of hexachloroethane. However, based on the literature available a number of needs can be proposed. These include: 1) dose/effect responses for plants (direct and indirect), soils, and microbial communities; 2) the influence of photolysis processes on hexachloroethane decomposition, particularly that on foliar and soil surfaces; and 3) a need to conduct detailed chemical characterization of feed materials, aerosols, and deposited materials to place any dose/response into perspective.

This report presents detailed results associated with the formation, transport, atmospheric transformation, deposition, and terrestrial ecological effects of hexachloroethane smokes. The research described is similar in nature to that performed with red phosphorus/ butyl rubber and white phosphorus smokes (Van Voris et al. 1987) and fog oil obscurants (Cataldo et al. 1988). The effects of aerosolized hexachloroethane on three primary ecosystem components were evaluated:

- natural terrestrial vegetation characteristic of U.S. Army training sites in the United States
- physical and chemical properties of soils at those sites
- soil microbiological and soil invertebrate communities.

2.0 MATERIALS AND METHODS

Tests of hexachloroethane (HC) smoke were conducted at the Aerosol Wind Tunnel Research Facility at Pacific Northwest Laboratory (PNL). This facility, which is located on the U.S. Department of Energy (DOE) Hanford Site in southeastern Washington State, contains an environmental wind tunnel suitable for testing obscurant smoke under a variety of environmental conditions. The facility, shown in Figure 2.1, and supporting laboratories are used for research involving generation, transport, deposition, and characterization of aerosols and gases in complex atmospheric environments. A more detailed description of the wind tunnel is provided in Section 2.1, and additional information can be found in Van Voris et al. (1987) and Ligotke et al. (1986).

2.1 AEROSOL WIND TUNNEL RESEARCH FACILITY

The PNL Aerosol Wind Tunnel Research Facility was constructed and supplied with a combination of special capabilities to provide laboratory simulation of natural environments. Tests are performed to test the transport, deposition, resuspension, and chemical fate of airborne particles and gases. While the advantages of laboratory tests over actual field tests include controlled and reproducible (on-demand) test conditions, shorter duration projects, and cost-effective methods of providing large quantities of usable data, it is of critical importance that such studies be performed in dynamic conditions provided by wind tunnels rather than in static or stirred exposure chambers. This is because of several conditions that are influenced by a dynamic environment: 1) contaminant aging in natural environments may include chemical and physical transformations that may be influenced by sunlight, humidity, temperature, or other parameters; 2) deposition of airborne particles, whether by diffusive or inertial forces, to test surfaces such as plants, soils, and water, is strongly influenced by wind speed and the flow field generated within plant canopies or the boundary layers of wind over leaves and other surfaces; and 3) the chemical fate of particles deposited to surfaces, or the rate of transfer of contaminants from the surface to the interior of plants and soils may be altered by the aging of surface deposits under the influences of temperature, humidity, and wind speed. Under static conditions (chambers with no uniform air flow, either with or without temperature and humidity control) transport, transformation, and effects of airborne materials will not likely be similar to those occurring in actual field environments. The dynamic conditions created in the wind tunnel during tests provides realistic simulation of natural environments for transport, transformation, and fate-and-effects experiments.

The laboratory of the research facility houses a sealed, recirculating (or closed-loop) wind tunnel, controlled-environment plant growth chambers, instruments for aerosol characterization, and a computer system, and is supported by a variety of analytical chemistry

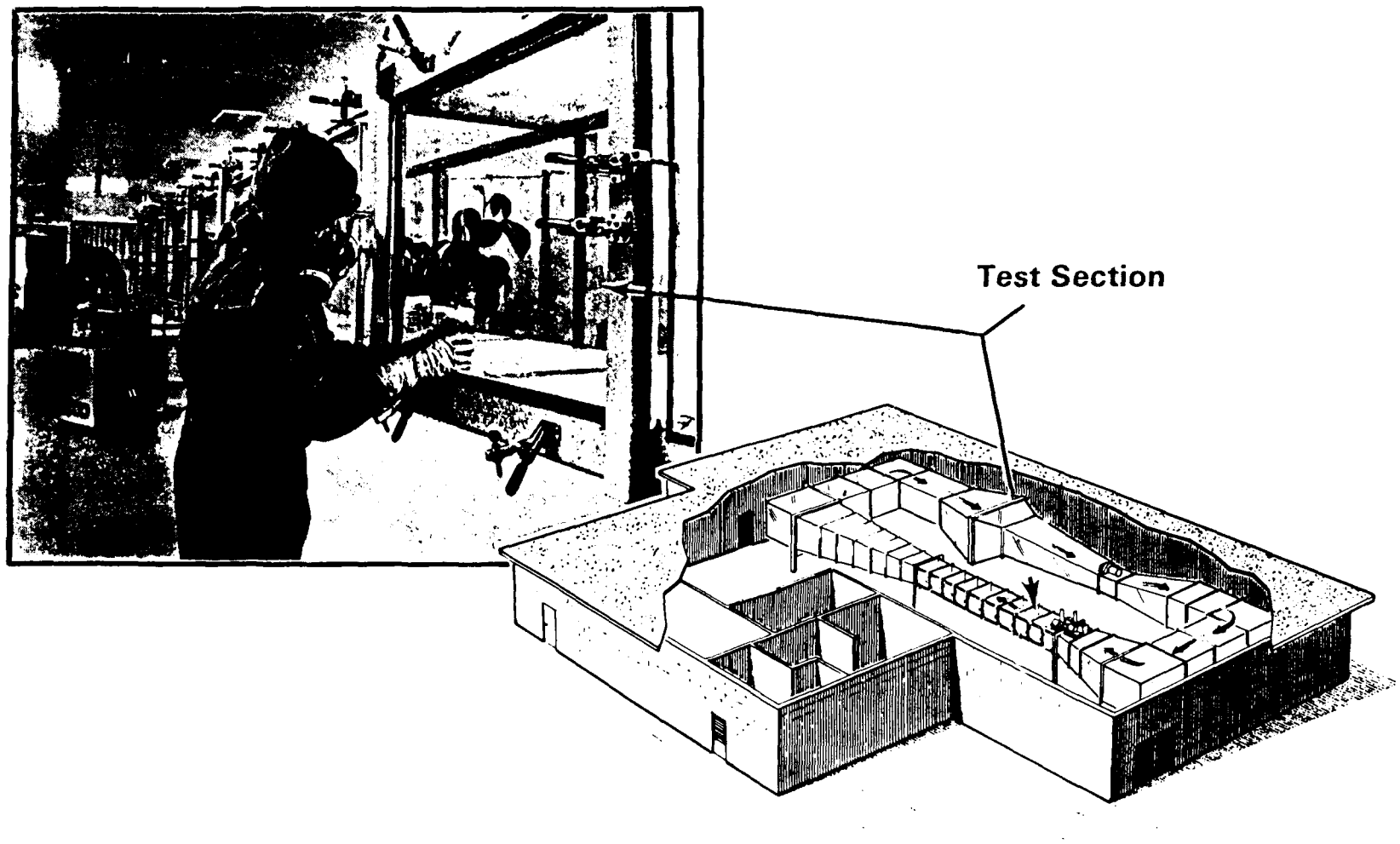


FIGURE 2.1. PNL AEROSOL WIND TUNNEL RESEARCH FACILITY

laboratories. Designed for total containment of airborne toxic, hazardous, and radioactive materials, the facility offers an unique capability to conduct aerosol research on such materials in a dynamic environment simulating natural field conditions. Computerized control of and data acquisition for the wind tunnel exposure environment include temperature, humidity, illumination, wind speed, gas species concentration, and airborne contaminant composition and dispersion.

The laboratory of the facility is supplied with filtered ambient air for ventilation; an independent exhaust system then draws this single-pass air through double banks of HEPA "absolute" filters before release. The negative air balance thus maintained within the facility by the exhaust system is protected by the presence of an emergency back-up diesel generator. In the event of a power failure, the back-up system operates to maintain complete containment of test materials.

The wind tunnel and other chambers are located within the laboratory, and are isolated from personal and mechanical rooms by an air lock. The wind tunnel is operated at a negative air pressure during tests to contain contaminants; however, as a precaution, staff are provided supplied-air breathing air systems as necessitated by specific requirements of particular experiments. The breathing air system provides air free of particulate and organic contaminants and contributes to safe working conditions.

2.1.1. Environmental Wind Tunnel

The environmental wind tunnel located within the PNL Aerosol Wind Tunnel Research Facility is used to study the transport, deposition, and chemical fate of airborne contaminants on physical and biological systems (Figure 2.2). Examples of the research areas addressed in the wind tunnel to date include: obscurant smokes (RP/BR, WP, FO, HC, and mixed smokes), pesticides, dusts and powder dispersion, scale model velocity profiles, boundary layer heat transfer, and wind erosion. Other tasks anticipated in the future include: transport and survivability of genetically engineered microorganisms, acid fog, atmospheric scavenging, and surface/air exchange of particulate and gaseous contaminants. The wind tunnel is ideally suited to environmental studies because of its large, 68-m^3 (2400-ft^3) volume, and because it is insulated and supplied with environmental control systems. Temperature is controlled by an air conditioning system; relative humidity is controlled by computerized injection of water vapor via an ultrasonic atomizer; and gas concentrations may be controlled by computerized monitoring and injection.

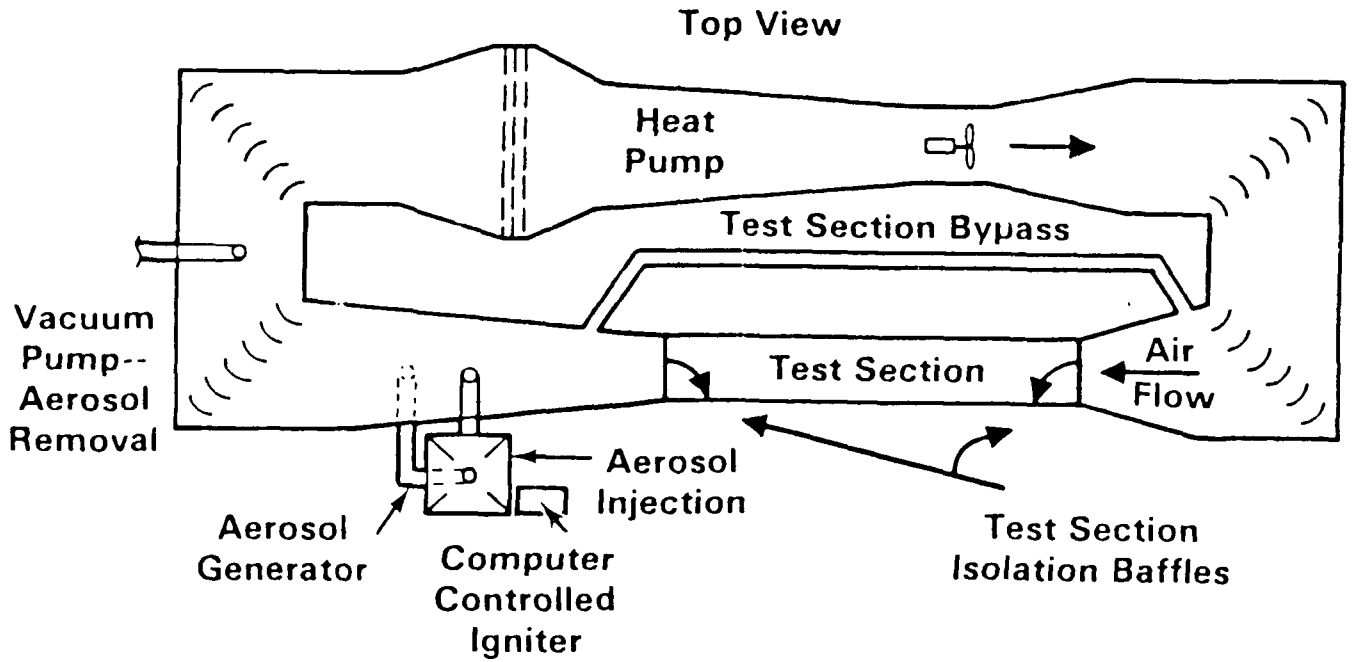


FIGURE 2.2. CLOSED-LOOP WIND TUNNEL, HC SMOKE GENERATION AND INJECTION, AND PRIMARY TEST SECTION

The wind tunnel is constructed of stainless steel and transparent Lexan® for resistance to chemical corrosives. A 300-psi washdown system is used to clean and decontaminate the wind tunnel following tests. Constructed as a closed-loop system as shown in Figure 2.2, the wind tunnel may also be operated in single-pass mode for many research applications by installing a 48-ft^2 bank of HEPA filters in the return section, just upwind of the 30-hp belt-driven fan. Because of the low pressure drop across the large area of the filter bank, the maximum attainable speed in the primary test section is 31 m/s (70 mph) with or without installation of the HEPA filters. Secondary test sections provide alternative test locations to the 0.6-m-square primary test section; two 1.5-m-square and one 2-m-square test sections may be used for large test subjects.

2.1.2 Wind Tunnel Test Section

The primary test section of the wind tunnel is 6.1 m long and 0.6 m wide and tall with transparent Lexan walls and ceiling (see Figure 2.1). Mean wind speed is controllable between 0.2 and 31 m/s (0.5 and 70 mph). Uniform air flow is provided by reducing boundary layer depths at the inlet to the test section using a specially shaped effuser section and turning vanes in all corners of the wind tunnel. Velocity is uniform over the center 85% of the test section cross section, and velocity gradients are typically less than 4%. Because aerosol generation is usually performed downwind of the test section, mixing is complete and uniform contaminant concentrations are provided to test subjects. Illumination is provided to maintain plant respiration processes; four adjustable 400-W metal halide lamps are mounted above the test section, and UV lamps are also available. Plant pots and other portions of test subjects that do not require exposure are placed below the surface of the test section floor within a false floor that is 4 to 9 in. deep.

To facilitate the performance of certain tests, isolation baffles are installed on the inlet and outlet planes of the test section. Upon completion of a test, these isolators are rotated upward to seal the test section from the rest of the wind tunnel. The air within the test section is then quickly cleared by purging it with clean, filtered laboratory air, thus providing a controlled end-of-test or providing an opportunity to access the test section and exchange test subjects for a second or continued exposure test. During the time the test section is isolated, a bypass duct is operated, thus maintaining the atmosphere in the remainder of the wind tunnel in a dynamic state. Because the volume of the primary test section is only 5% of the total wind tunnel volume, similar tests may be performed in series by reopening the test section and continuing the exposure test immediately without the need to recreate the test atmosphere.

2.1.3 Aerosol Instrumentation

A complete inventory of instrumentation is available to monitor the test environment (including gas composition) and aerosol concentration, particle size distribution and shape, and chemical composition. A computer control and data acquisition system is used to operate experiments and document monitoring instrument data and status. The system provides flexibility to operate during a wide variety of experiments and provides alarms to alert the operator if specific conditions or aerosol characteristics are not maintained within preset tolerances.

In addition to aerosol measuring devices, aerosol generators are available for the generation of most types of suspended particulate contaminates. A partial list of aerosol generators available at the facility includes: combustion and vaporization/condensation for pyrotechnically generated materials, nebulizers, foggers, and ultrasonic sprayers for liquid sprays, energy mills and fluidized beds for dispersion of powders and dusts, vibrating orifice and spinning disk generators for monodisperse calibration aerosols, and other devices developed for specific generation needs.

In addition to monitoring the suspended contaminant, other aspects of the exposure environment are monitored. Wind speed is measured using hot film anemometry or by employing a state-of-the-art differential pressure transducer connected to standard pitot-static probes. Temperature and relative humidity are measured in the wind tunnel and at other locations using connected thermocouples and optical dew point sensor systems. The concentrations of specific gas or vapor species may be monitored by a collection of analyzers (O_2, CO_2, CO, SO_2, NO_x, O_3, and tunable IR), and other gases and vapors are also analyzed using an on-line gas chromatograph.

Aerosol mass concentrations between <0.01 mg/m^3 and >10 g/m^3 are measured using isokinetic filter samples, laser transmissometers, and single- and multiple-particle light-scattering devices. Physical samples are analyzed gravemetrically, or by chemistry, fluoroscopy, or optical or SEM microscopy. Particle size distributions of airborne contaminants are measured for particles with diameters ranging from 0.003 to 450 μm using a variety of instruments employing inertial, diffusive, optical, and electrical mobility classifying procedures. One analyzer sizes and counts particles remotely using a pair of He-Ne laser beams. That device provides the advantages of analyzing particles without the use of a physical probe that may influence air flow and particle deposition patterns, rapid (real-time) analysis of airborne material, and reduced need to remove toxic and hazardous materials from the wind tunnel for analysis. Techniques for characterization of nonspherical particles such as fibers and chain-agglomerates have also been developed.

2.1.4 Analytical Chemistry

In addition to the size and concentration of airborne particulate contaminants within the wind tunnel, it is important to characterize the chemical form of the particles. While many aerosols such as some ash, dust, and metal aerosols are relatively chemically stable, most aerosols are transformed chemically between generation or suspension and deposition. Because of this, aerosol samples and samples from deposition coupons and plant, soil, water, and other test subjects are analyzed by chemical methods. Chemical analytical methods employed in these studies included: high pressure liquid chromatography (HPLC), gas chromatography (GC), gas chromatography/mass specrometry (GC/MS), anion chromatography (AA), inductive coupled argon plasma spectrometry (ICAP), and others.

2.2 EXPOSURE CONDITIONS

The exposure environment within the wind tunnel was controlled. Both wind speed and relative humidity were varied as test parameters. Concentration of HC aerosol and time of exposure were also controlled to provide test conditions. Temperature was monitored, but not varied as a test parameter for HC tests. The environmental and aerosol conditions occurring during tests were monitored and recorded using the computer system and other devices such as isokinetic samplers, cascade impactors, and particle impingers. After setting the test environment just before each test, HC aerosols were generated using miniature HC smoke pots and introduced into the wind tunnel downwind of the test section. Continued generation of HC aerosols was performed at regular intervals during the tests to maintain relatively consistent, stable aerosols over periods of several hours.

2.2.1 Exposure Environment

Environmental parameters in the wind tunnel were controlled to closely match those existing in the field. Air temperature was constant and between 20°C to 23°C during most tests. The relative humidity of the wind tunnel atmosphere was controlled and ranged from 20% to 85% depending on specific test requirements; water vapor was added to the system to maintain the higher humidities. Tests were performed at wind speeds of 0.9, 1.8, 2.7, and 4.5 m/s (2 to 10 mph).

The humidity of the wind tunnel atmosphere was typically measured during each test using a General Eastern Model 1500 Hygrocomputer. Samples were drawn from the wind tunnel continuously during each test through a Teflon® -substrate filter suspended in the wind tunnel downwind of the test section. The filter was protected from carbon and particulate deposits by a plastic sheath on the upwind side. The dewpoint sensor was cleaned

periodically. The hygrocomputer was also used to measure wind tunnel temperature, and was calibrated by comparison with a precision controlled-draft sling psychrometer.

The mean, or average, wind speed approaching the test subjects in the wind tunnel test section was measured using a Thermal Systems Incorporated (TSI) hot-film probe Model No. 1366 connected to a TSI Model No. 1054A anemometer. This device was calibrated by comparison with a pitot-static probe, a laboratory standard for air velocity measurement. The pitot-static tube was positioned centerline in the wind tunnel test section and connected to a Dywer Model No. 1430 micromanometer. This procedure provided calibration of the hot-film probe at a location just upwind of the test section.

2.2.2 Test Procedures and Measured Conditions

Because physical and chemical characteristics of aerosols change as they age following generation by combustion, HC aerosols were introduced into the wind tunnel continuously (miniature HC pots were ignited at 20- to 30-min periods throughout each test) and allowed to age during the exposure tests. Use of the dynamic exposure environment within the wind tunnel provided close representation of field conditions. Use of static test chambers was avoided because of the need to reproduce particulate HC deposition characteristics, which are influenced by wind speed and air flow patterns in plant canopies. To prevent aging of the HC aerosols in the wind tunnel, a flow of carrier air was provided to the aerosol generation chamber to transport the aerosol into the wind tunnel, and an equivalent flow was drawn out of the wind tunnel. This transfer flow rate was 20 cfm and resulted in a net loss of aerosol from the wind tunnel system of 1% per minute. Aerosol losses by deposition to the test subjects and the surfaces of the wind tunnel accounted for an additional ~1% per minute. The HC aerosol was therefore a mixture of freshly generated and aged particles; this experimental laboratory approach was followed to provide field conditions. Based on the residence time within the wind tunnel, the average age of the HC aerosol in the wind tunnel was to be about 40 min, or similar to that of a field-generated aerosol that had drifted approximately 2 km downwind under the influence of a slow 0.9 m/s (2 mph) wind.

The duration of the exposure interval for each wind tunnel test was based on transmissometry of smoke density. Test start times were nearly instantaneous and thus easily estimated. The test section was bypassed before each test until a constant concentration of the aerosol was present in the wind tunnel, with the test section isolated and containing fresh air. The time required to attain steady-state concentrations ranged from 20 min to 30 min. At that time, the exposure was begun by allowing HC smoke to pass through the test section and closing the bypass loop (see Figure 2.2). Aerosol generation continued until the test was finished, at which time the test section was again isolated and flushed with fresh air. Because

approximately 5 min were required to flush the visible smoke from the test section at the end of each test, the end of the exposure test was assigned to that time when the test section purge was one-half complete, which was typically 2 or 3 min after initiation of test section purging.

Exposures were typically 1, 2, 3, or 4 h in length. Each test consisted of a single exposure to HC obscurant smoke. Tests were performed for instrument calibration and HC aerosol generator performance. These were in addition to the four experimental test series designated as range finding, wind speed, relative humidity, and cumulative dose. Chemical analysis of HC aerosols, a fifth testing category, was primarily conducted during the relative humidity and cumulative dose tests. Conditions measured during tests are listed in Table 2.1. The range-finding tests included exposures of 1, 2, 3, and 4 h duration. Wind speed tests were performed at 0.9, 1.8, 2.7, and 4.5 m/s (~2 to ~10 mph). Four relative humidity tests were completed, the first three at 20, 55, and 85%, and a fourth at an average humidity of 66% with an intermittent precipitation event occurring during the second half of the test (during which time the wind tunnel relative humidity averaged 77%). Two series of cumulative dose tests were performed simultaneously. In both series, test subjects were exposed to nine tests over a 3-week period.

Some measurements of humidity, wind speed, and test duration were limited to secondary measurement devices due to failure of primary devices. Relative humidities were approximated during the range-finding tests by measuring pretest humidity using a precision constant-draft sling psychrometer, because the optical dew point sensor had been returned to the manufacturer for recalibration. This method was judged to be satisfactory after other tests failed to show either a decrease or increase in humidity in the wind tunnel during test periods. Wind speed was measured by pitot-static probe connected to a certified micromanometer at the begining of some tests when the hot-film probe was not available. Because wind speed remains constant with time, this measurement was judged to be sufficient. Time of exposure was estimated using a secondary timer (not connected to the computer system) on two occasions when temporary power failures interrupted tests.

Wind speed data, including natural fluctuations in the wind tunnel air flow and measurement uncertainties, are presented in detail for the HC wind speeds tests in Table 2.2. The greatest deviation of measured wind speed from average was seen to be 11% at 0.9 m/s, 7% at 1.8 m/s, and 4% at 2.7 and 4.5 m/s.

Fluctuations in wind tunnel relative humidity occurred as steam was injected via a computer-controlled valve into both the wind tunnel and the aerosol generation system.

TABLE 2.1. ENVIRONMENTAL CONDITIONS, WIND SPEED, AND EXPOSURE DURATION FOR HC OBSCURANT TESTS

Test	Date	Temp. (~°C)	Relative Humidity (%)	Wind Speed (m/s)	Exposure Duration (min)
Range-Finding:					
HC-4-3	6/25/86	22.6	~40[a]	0.91	180
HC-5-4	6/26/86	21.8	~45[a]	0.90	235
HC-6-1	6/26/86	21.8	~45[a]	0.92	60
HC-7-2	6/26/86	22.1	~45[a]	0.89	120
Wind Speed:					
HC-9	7/23/86	~22.0	~50[a]	4.50	60
HC-11	9/23/86	21.1	53	0.89	120
HC-12	9/23/86	22.2	58	1.79	121
HC-13	9/25/86	20.5	69	2.79	120
HC-14	9/25/86	21.9	62	4.53	120
Relative Humidity					
HC-16	11/3/86	23.3	20	0.88	240
HC-17	11/5/86	23.2	55	0.89	240
HC-18	11/11/86	22.2	85	0.89	240
HC-19	11/17/86	21.4	66[b]	0.91	240
Cumulative Dose:					
HC-22[a]	2/9/87	22.7	~40	0.88	180
HC-22[b]	2/9/87	22.7	47	0.88	180
HC-23[a]	2/11/87	21.9	54	0.88	180
HC-23[b]	2/11/87	22.8	56	0.88	180
HC-24[a]	2/13/87	21.1	52	0.89	180
HC-24[b]	2/13/87	22.4	52	0.89	180
HC-25[a]	2/17/87	21.1	52	~0.90	180
HC-25[b]	2/17/87	21.8	53	0.90	180
HC-26[a]	2/18/87	21.1	53	0.90	180[c]
HC-26[b]	2/18/87	21.8	53	0.89	180
HC-27[a]	2/20/87	21.4	57	0.90	180
HC-27[b]	2/20/87	22.2	55	0.87	180
HC-28[a]	2/23/87	21.0	58	~0.90	~180[c]
HC-28[b]	2/23/87	21.6	60	0.88	180
HC-29[a]	2/25/87	20.9	53	0.94	180
HC-29[b]	2/25/87	21.3	52	0.95	~180[c]
HC-30[a]	2/27/87	20.6	54	~0.90	179
HC-30[b]	2/27/87	21.6	53	~0.90	180

(a) Humidity was measured before tests using a constant-draft sling psychrometer.
(b) Simulated rainfall was generated during the second half of HC-19. Humidity increased from 55 to 77%.
(c) Incomplete data record because of power failure.

Because of the large volume of the wind tunnel, these fluctuations were not large relative to the average humidity during each test. Table 2.3 lists average relative humidities during the relative humidity test series tests. The standard deviation of data collected by the computer system was seen to be less than 5% for all tests, including the relative humidity test series, with the exception of test HC-19 (the test with simulated rainfall occuring during the second half of the test). Figure 2.3 shows the relative humidity histories for the relative humidity test series tests.

TABLE 2.2. MEAN WIND SPEED DURING WIND SPEED TESTS WITH HC AEROSOLS. SENSOR CALIBRATION SHIFTS, REAL VELOCITY FLUCTIONS, AND MEASUREMENT UNCERTAINTIES CONSIDERED

Test No.	Target (m/s)	Measured (m/s)	Calib. (m/s)	Actual (m/s)
HC-11	0.90	0.90	-0.015	0.89 ± 0.10[a]
HC-12	1.79	1.79	-0.005	1.79 ± 0.13
HC-13	2.69	2.69	+0.10	2.79 ± 0.11
HC-14	4.48	4.33	+0.20	4.53 ± 0.18

(a) Uncertainty equals the maximum observed deviation from average during pre-test and post-test calibration measurements.

TABLE 2.3. RELATIVE HUMIDITY AVERAGES DURING RELATIVE HUMIDITY TESTS WITH HC AEROSOLS. SENSOR CALIBRATION SHIFTS, REAL VELOCITY FLUCTIONS, AND MEASUREMENT UNCERTAINTIES CONSIDERED

Test No.	Temp. (°C)	Target (%)	Measured (%)	Uncertainty (%)[a]
HC-16	23.3	20	20	± 0.72 (n=110)
HC-17	23.2	60	55	± 1.09 (n=150)
HC-18	22.2	90	85	± 0.98 (n=111)
HC-19	21.4	[b]	66	± 12.1 (n=112)[b]

(a) Uncertainty equals the standard deviation of n samples.
(b) Large standard deviation resulted from the generation of simulated rainfall during the second half of test HC-19. RH increased from 55 to 77% during that test.

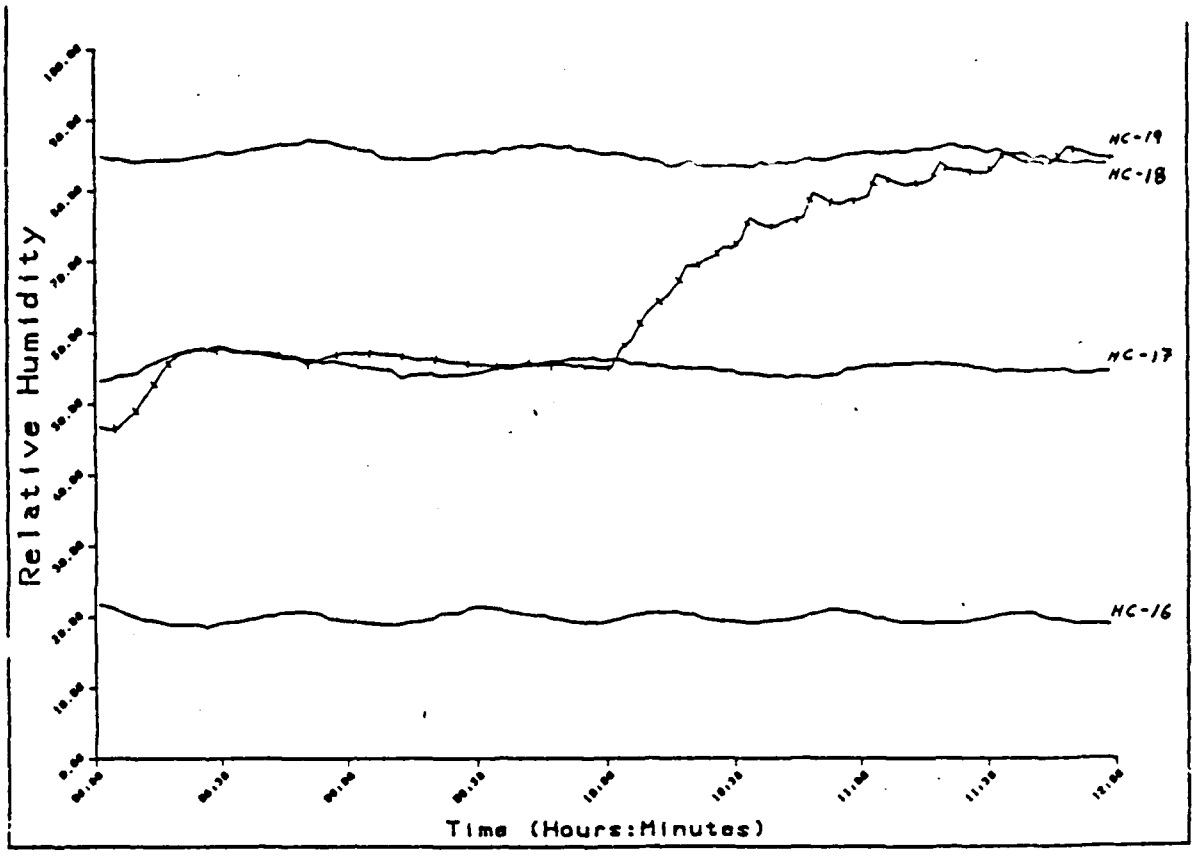


FIGURE 2.3. RELATIVE HUMIDITY VERSUS TIME FOR EACH OF THE HC RELATIVE HUMIDITY TESTS. TEST HC-19 SHOWS INCREASING HUMIDITY DURING THE SECOND HALF OF THE TEST CAUSED BY GENERATION OF SIMULATED RAINFALL

2.3 SMOKE (AEROSOL) GENERATION

HC aerosols were generated and introduced into the wind tunnel continuously during each test to maintain steady-state aerosols of constant physical and chemical characteristics for measurements of transport, transformations, and effects on plant, soil, microbe, and other test subjects. Scaled-down versions of standard 30-lb HC smoke pots were developed and ignited under computer control at 20- to 30-min intervals throughout each test.

2.3.1 Test Materials

Materials used to prepare minature HC pots included hexachloroethane (HC), zinc oxide, and aluminum powders. Two mixtures of the powders were used in the construction of each HC pot. The top 20% of each pot was prepared using a mixture containing an increased amount of aluminum powder (9% starter mixture) as compared to the lower 80% of the charge, which contained a mixture having 6% aluminum, by mass. The mixture with 9% aluminum was labeled mix HC-1, and that with 6% aluminum was labeled mix HC-2. In both mixtures the ratio of ZnO to HC was equal to 1.04. Fresh batches of both mixtures were prepared before each series of tests. Differences between minature HC pots and the 30-lb pots in the Army's inventory included size (a 20 g HC pot contains 0.15% of the charge of a 30-lb HC smoke pot), and composition-30-lb smoke pots contain a lesser fraction (less than 20%) of the high-aluminum mixture and also contain a thermite igniter. The small size of the miniature HC pots did not make feasible the use of a thermite starter, and the larger fraction of high-aluminum mixture was required to ensure that the hot wires used as starters would make contact with the mixture containing 9% aluminum. Other than during the range-finding tests, the HC mixture was contained in tin cans with only a 3/8-in.-diameter hole open at the top to simulate the geometry of the 30-lb HC smoke pots.

Tin, gill-style, cups with lids were used to contain the miniature HC pots pictured in Figure 2.4. Several can sizes were used (0.5, 1, and 2 oz); charges ranged from about 10 to 40 g of HC mixtures per pot. Can selection and use depended on the frequency of pot ignition and the desired HC aerosol concentration in the wind tunnel. HC pots were prepared by packing powder mixtures in the tin cups to a density of 1.75 ± 0.15 g/cm^3. A 3/8-in. circular hole was drilled into the center of each can bottom, a paper was used to cover the hole, mix HC-1 powder (starter mixture) was added to the container followed by mix HC-2 powder, the powders were compressed in a pellet press, and pure white-quartz sand was added to top of the container to act as a nonreactive thermal barrier. The lid was subsequently fit into place and taped closed. HC pots were inverted, with ignition hole up, when used. As the mixtures burned, a jet of dirty white smoke was emitted from the circular hole.

2.3.2 Aerosol Generation

Several trial tests were conducted before determination of suitable HC pot configuration and ignition procedures. Hot wires (10 A) used previously to ignite phosphorus compounds were insufficient to intiate combustion. Magnesium ribbon fuses initially showed promise as a starter, but were inconsistent and thus judged not to be suitable. HC pots were, however, ignited in open-face containers during the range-finding tests using magnesium ribbon fuses; open-face containers were used as the mixtures tended to smolder rather than burn in containers with only 3/8-in.-diameter access holes.

After the range-finding tests, the packing configuration described above was developed that resulted in powder packed up to the level of the circular hole and eliminated the void space above the powder surface in earlier trials. To eliminate the inconsistency of the magnesium ribbon fuses, a larger hot-wire system was developed. Nichrome hot wires operated at 30 A were found to be sufficient to produce sufficient temperature to initiate combustion. A system of 20 hot wire ignition stations was developed; these were automatically sequenced by the computer control system for each test.

Before each test, HC pots were placed into the ~3-m^3 buffer tank of the aerosol generation system and prepared for ignition. Each HC pot was placed on a sand surface in a stainless steel tray and connected to a hot-wire starter. Contact was made between the HC pots and the starter wires by piercing the protective paper and inserting the wire about 0.5 cm into the compacted HC charge. The chamber was then sealed and the generator system powered.

Hot wires were energized for 20 to 30 s to initiate combustion. HC pots burned vigorously and emitted a dirty white plume as well as flaming ash. Figure 2.4 shows an ignited HC pot. Temperature measurements made with a thermocouple during several combustion sequences indicated a temperature of 620°C was developed rapidly--within 3 or 4 s--and remained constant throughout the duration of the 10-to 13-s combustion period. During combustion the tin containers were observed to become red and glow. Smoke from each HC pot was premixed in the buffer tank to provide uniform smoke concentrations, and then drawn into the wind tunnel, downwind of the test section. Because the time required for cycling air within the closed-loop wind tunnel ranged from 0.5 to nearly 3 min, freshly generated HC aerosol mixed with the wind tunnel atmosphere before passing through the test section. Thus temperature gradients were not present in the test section and aerosol mass concentration was uniform.

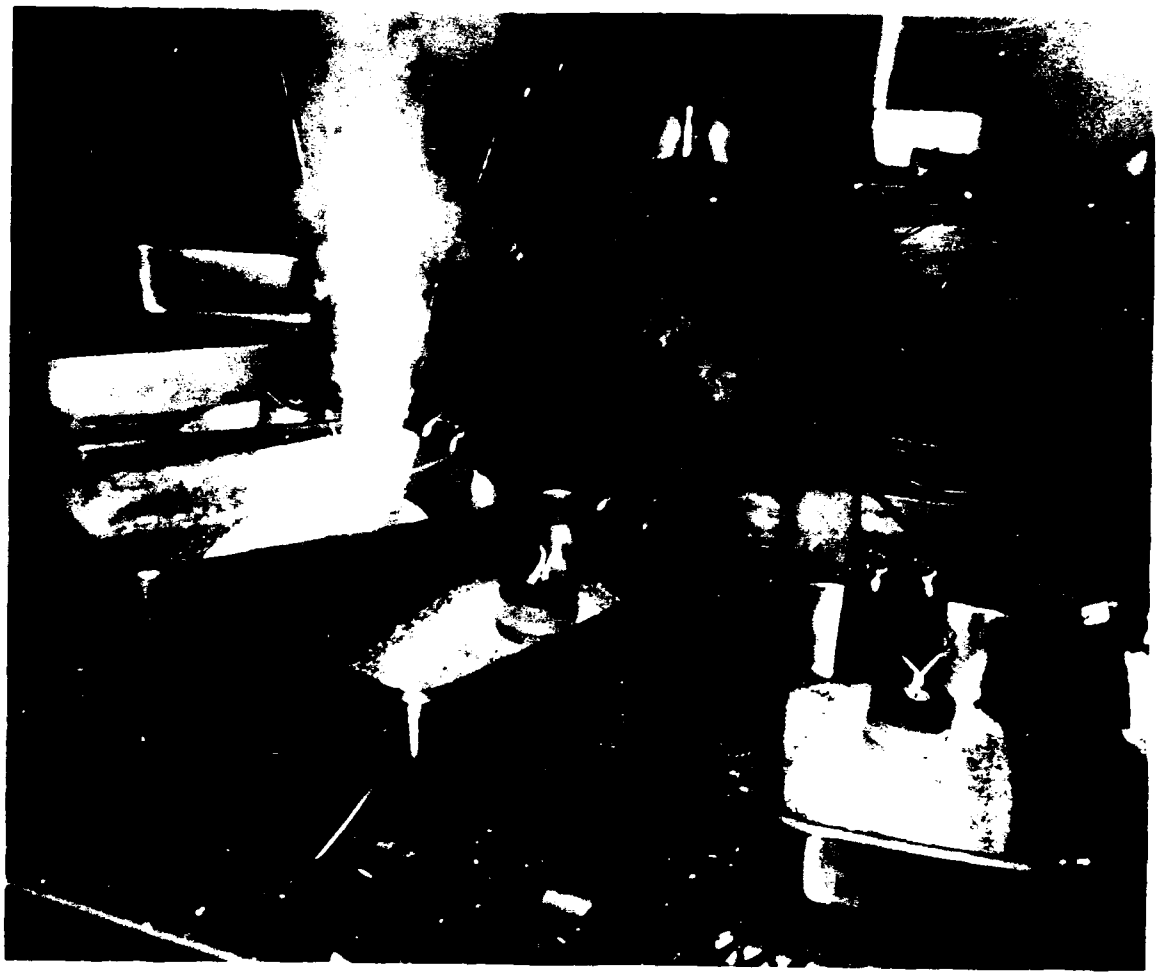


FIGURE 2.4. HC POT GENERATING SMOKE IN THE AEROSOL GENERATOR BUFFER CHAMBER

2.4 SMOKE (AEROSOL) CHARACTERIZATION

Hexachloroethane (HC) aerosols were produced in the wind tunnel, and are produced in the field, by burning a mixture of powders, as described in Section 2.3. While particles in HC aerosols consist primarily of zinc chloride and carbon, smaller amounts of aluminum and

chlorocarbon compounds are also present. In addition, especially the lower molecular weight chlorocarbons such as carbon tetrachloride and ethylene tetrachloride are present in the aerosol both condensed onto particles and as vapors. The specific chemical composition of the suspended particles likely depends on conditions at generation, the presence or absence of water vapor, and the duration of the aging process. An effort was made to reproduce actual field combustion conditions during the wind tunnel tests; the material was burned rapidly with an intense flame. Smoldering was limited to a very short period immediately following generation of the smoke. The influence of different rates of combustion on aerosol chemistry, which could be performed by reducing oxygen fractions, was not investigated.

HC aerosols were characterized during each test in the wind tunnel. Measurements were made so that aerosol mass concentration, particle size distribution, and chemical composition could be determined. Mass concentration and particle size distribution are important characteristics of aerosols and affect the dose and effects of HC on the environment. Mass concentration of suspended particles is the characteristic most directly linked to the bulk dose, or mass loading of HC to environmental surfaces such as plants, soil, and water. Particle size distribution has an important influence on the transport and on deposition rates. Large particles deposit more readily under the influence of wind speed and gravitational force, while small particle transport and deposition were governed by diffusional forces. In addition to physical characterization of HC aerosols, the chemical composition of HC aerosols was measured to determine relative levels of specific components of the aerosol, for both airborne and deposited particulate matter. Analyses of data provided information for specific times during the exposures and for the average of aerosol characteristics over the duration of each test. In addition, surrogate surfaces were analyzed to determine the rate of particle deposition, or deposition velocity, for comparison with plant, soil, and water surfaces.

2.4.1 Aerosol Mass Concentration

Aerosol mass concentration during HC tests was measured at 30- to 60-s intervals using a laser transmissometer consisting of a 2-ft-pathlength He-Ne laser (633 nm) oriented just upwind of the test subjects located in the wind tunnel test section. Because the response of the laser transmissometer to HC aerosols was a function of the optical characteristics of the suspended particles (which were in turn influenced by the concentration, size, and composition, and by test conditions such as relative humidity), the system was calibrated during each test by comparison with isokinetic filter samples. The filter samples were obtained by drawing quantities of the wind tunnel atmosphere through a sharp-edged nozzle and collecting the particulate matter in the sample on glass fiber filters. The filter samples satisfied isokinetic requirements and collected particles efficently from the wind tunnel. A photograph of the laser beam of the transmissometer is shown in Figure 2.5.

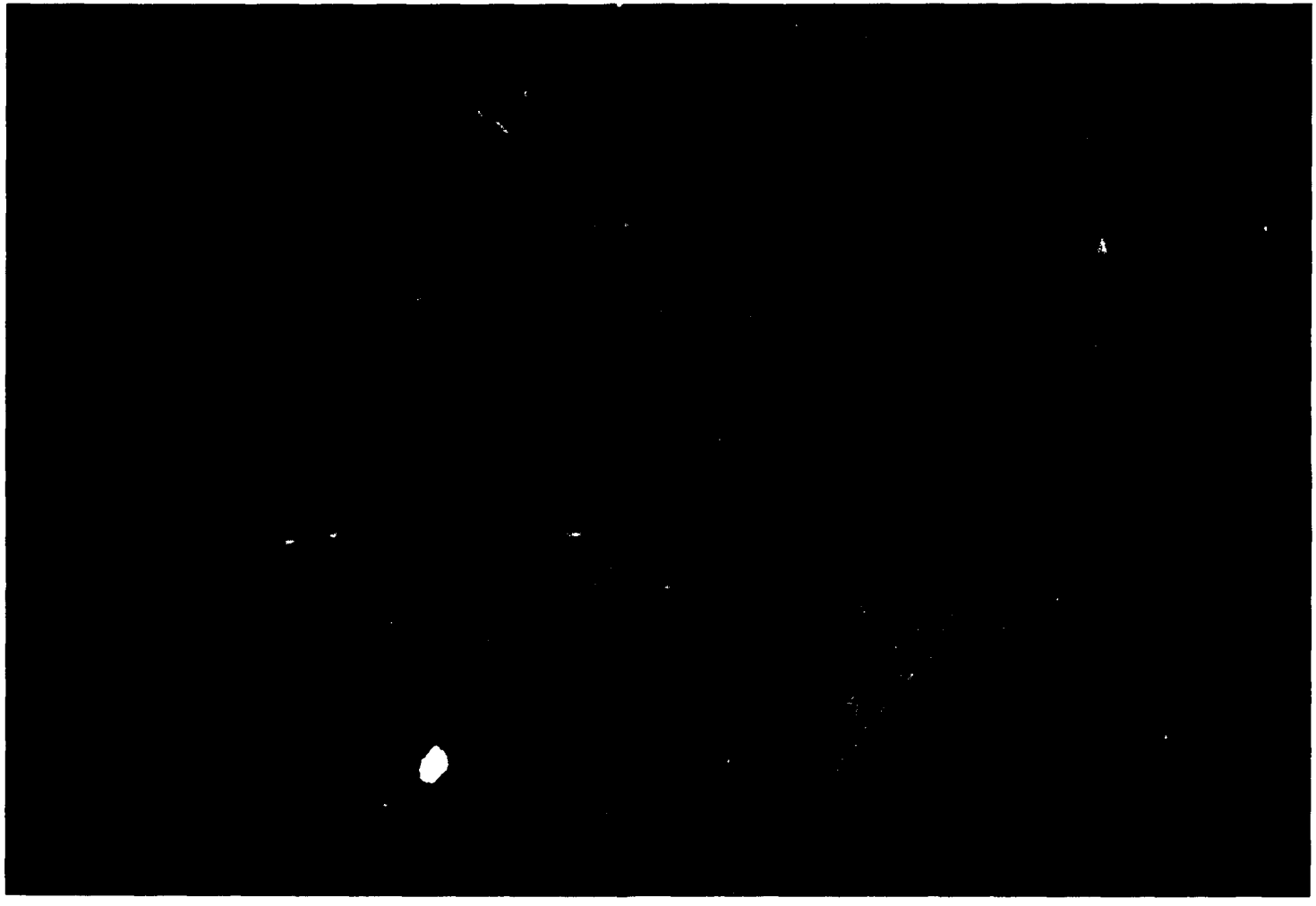


FIGURE 2.5. LASER TRANSMISSOMETER USED TO MEASURE ACTUAL AEROSOL MASS CONCENTRATION IN THE WIND TUNNEL TEST SECTION

The configuration of the isokinetic sampling system was slightly different than previous (RP/BR, WP, and FO) tests; the collection filter was located outside of the wind tunnel rather than immediately behind the nozzle. Between the sampling nozzle and the collection filter of the isokinetic sample was a smooth-walled tube with a gradual bend of 90°. While designed to maximize the transfer of particles to the collection filter, some fraction of the particulate mass was anticipated to be lost in the transfer. Because of this, the sampling effectiveness of the isokinetic system was measured during calibration tests HC-20 and HC-21. The smooth-walled tube was cleaned and then used to sample an HC aerosol in the wind tunnel. The inner surfaces of the nozzle and sampling tube were then rinsed with dilute nitric acid and the total amount of zinc measured was compared to the total amount of zinc collected on the filter plus that in the nozzle and sampling tube. This provided a measure of the effectiveness of the isokinetic sampling system and, after repeated measurements at the various wind speeds and nozzle sampling rates used during the HC tests, a range of probe sampling effectiveness was determined. Multiple rinses were performed to ensure complete removal of zinc from the sampling system after each sample, and the efficiency of the first rinse was shown to be 90.0 ± 2.6%. Other than a limited number of samples obtained at incorrect flow rates, the range of sampling system effectivenesses ranged from ~70% at 0.9 m/s to 88% at 1.8 m/s, 91% at 2.7 m/s, and 94% at 4.5 m/s. The relationship of losses to sampling flow rate indicated that deposition of particles, rather than impaction in the gradual bend, accounted for most of the sampling losses. An analysis of the need for isokinetic sampling revealed that sampling HC aerosols at twice the isokinetic rate during tests at 0.9 m/s would be appropriate to reduce deposition losses. The super-isokinetic sampling rate was used for most measurements at 0.9 m/s, and the probe effectiveness for this condition was found to be 88%. Correction factors for aerosol mass data were calculated from the sampling probe effectiveness measurements and were 1.14 for tests at 0.9 and 1.8 m/s, 1.10 at 2.7 m/s, and 1.06 at 4.5 m/s.

A series of isokinetic samples were obtained during each test to provide calibration information for the laser transmissometer. These samples were weighed immediately and then either contacted with isooctane for determination of organic constituents or desiccated for subsequent reweighing and selected contact with dilute nitric acid for determination of inorganic constituents. Mass concentrations were determined by comparing the fresh, desiccated, or chemical (Zn, Al, Mg, . . .) masses measured on the filter substrates with the total volume of wind tunnel atmosphere sampled. Appropriate sampling probe effectivenesses correction factors were applied to the data from each test through test HC-19 after determination of uncorrected aerosol mass concentration using transmissometer data. Because of consistent test and sampling procedures, a constant probe correction factor, 1.12, was applied to the data before plotting the transmissometer data for the cumulative dose tests (HC-22 through HC-30).

TABLE 2.4. LINEAR CALIBRATIONS DETERMINED FOR A He-Ne LASER TRANSMISSOMETER FOR EACH OF THE HC AEROSOL EXPOSURE TESTS. Form of Equation: $y = mx + b$. (Aerosol Mass Concentration [y], Transmissometer Output [x], Coefficient of Correlation [R^2], Number of Calibration Data Sets [n].)

Test	Probe Corr. Factor (-)	Slope (m)	Intercept(b)	Coef. of Corr. (R^2)	No. of Data Sets (n)
HC-4	1.12[a]	-4842	1107	0.98	10
HC-5	1 12[a]	-5167	1161	0.99	11
HC-6 & 7	1.12[a]	-5481	1086	0.94	11
HC-9	1.13[a]	-5899	1233	0.96	5
HC-11	1.24[a]	-3590	747	0.96	10
HC-12	1.28[a]	-2130	597	0.78	9
HC-13	1.17[a]	-4090	890	0.94	10
HC-14	1.05[a]	-4930	1060	0.94	8
HC-16	1.12[a]	-3941	1042	0.98	11
HC-17	1.12[a]	-6427	1155	0.97	12
HC-18	1.12[a]	-20652	2181	0.80	11
HC-19	1.12[a]	-12453	1448	0.99	11
HC-22	1.12[b]	-10798	1925	0.98	15
HC-23	1.12[b]	-7855	1619	0.99	16
HC-24	1.12[b]	-6757	1443	0.99	16
HC-25	1.12[b]	-7862	1449	1.00	16
HC-26	1.12[b]	-7018	1479	0.98	16
HC-27	1.12[b]	-7413	1523	0.99	16
HC-28	1.12[b]	-7728	1594	0.98	13
HC-29	1.12[b]	-6489	1384	.099	12
HC-30	1.12[b]	-7806	1559	.099	16

(a) Transmissometer calibration equations determined before probe correction factors (CF) were measured. Average aerosol mass concentrations determined for these tests using transmissometer data have been increased by Cm * CF.

(b) Transmissometer calibration equations for these tests include the aerosol sampling probe correction factor.

The output of the laser transmissometer was measured as the transmitted (2-ft-pathlength) laser power (Pt) divided by the output power (Po). Calibration functions, listed in Table 2.4, were determined for all tests and applied to the transmissometer data sets. These calibrations indictated a linear relationship between transmissometer output and aerosol mass concentation over the range of concentrations considered. Calibrations from selected tests are shown in Figures 2.6 and 2.7. Correlations with other parameters such as desiccated aerosol mass concentration were anticipated to be poor because of the dependence of transmittance on particle refractive index and size (both influenced by the amount of water associated with the particles) and were not employed. As expected, the transmissometer calibration for the

high relative humidity test HC-18 deviated from the norm, possibly because of the increased size and altered refractive index of the suspended particles from water absorption by the aerosols.

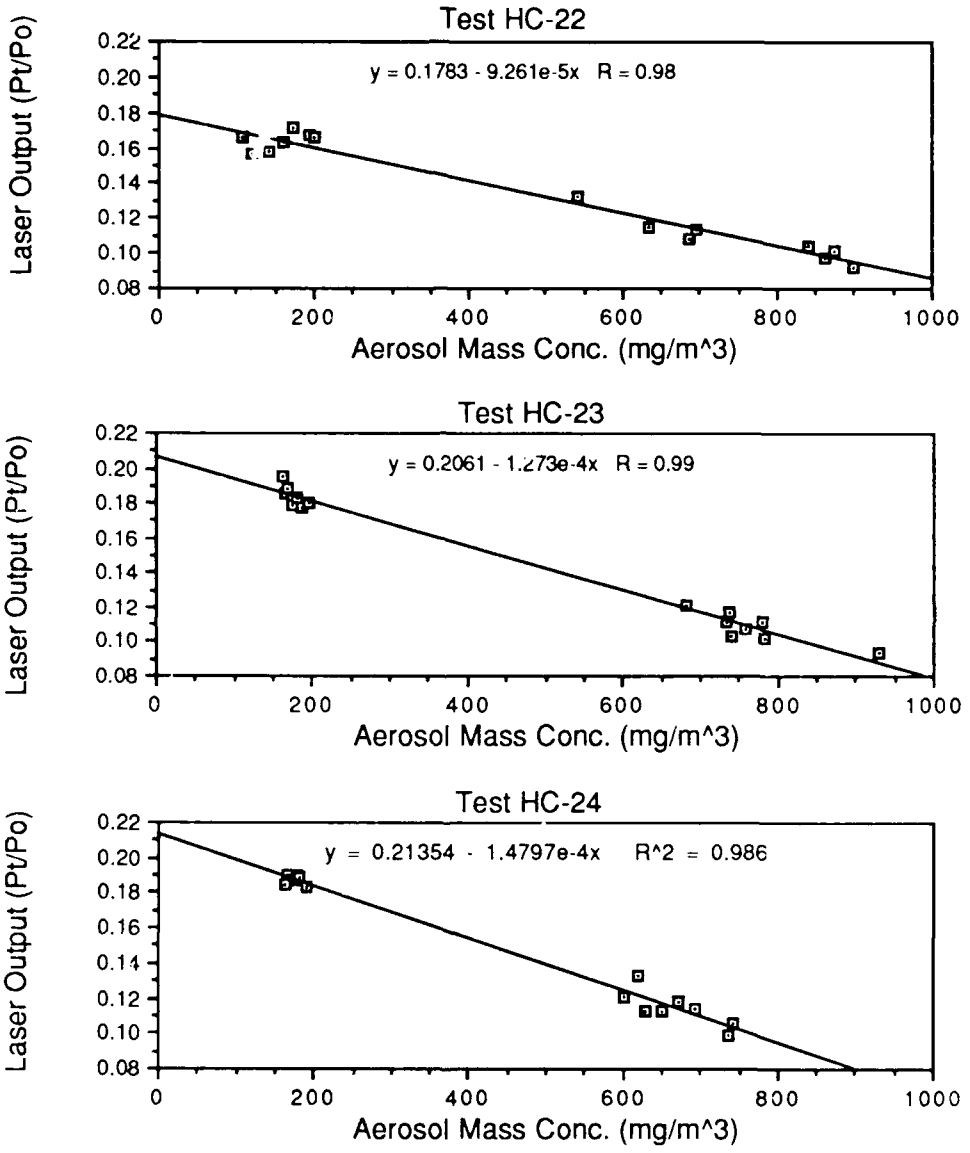


FIGURE 2.6. CALIBRATION RELATIONSHIPS FOR THE LASER TRANSMISSOMETER FOR TESTS HC-22, -23, AND -24

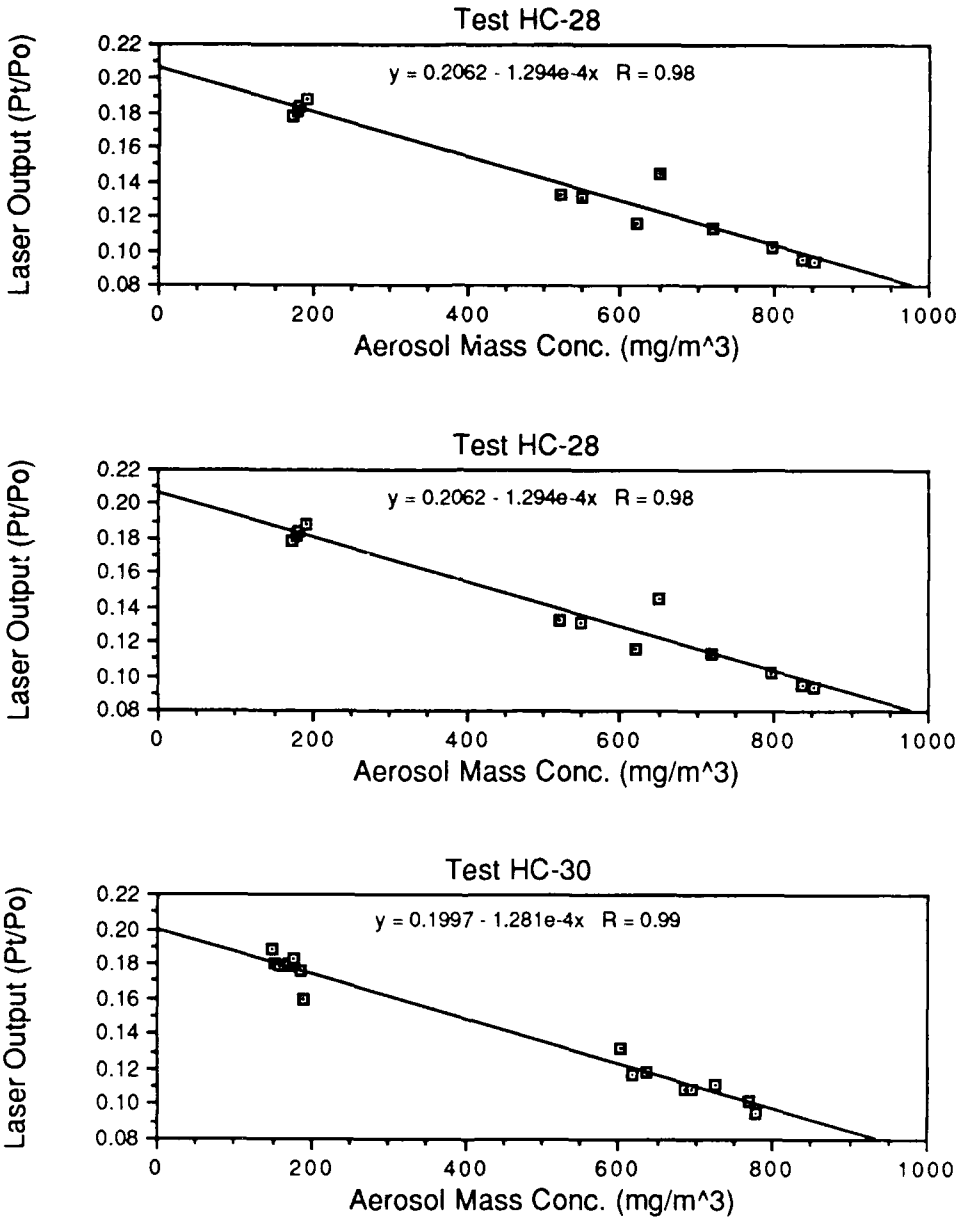


FIGURE 2.7. CALIBRATION RELATIONSHIPS FOR THE LASER TRANSMISSOMETER FOR TESTS HC-28, -29, AND -30

2.4.2 Particle Size Distribution

The size of particles that make up an aerosol often determine which forces, inertial or diffusive, control transport and deposition phenomena. The deposition velocity of particles to surfaces varies with the particle size; typically, particles with aerodynamic diameters between 0.1 and 1 μm deposit to natural surfaces such as plants, soil, and water less quickly than smaller or larger particles. This difference exists because even smaller particles are strongly affected by diffusive forces and larger particles by inertial forces. HC obscurant aerosols consist mostly of particles with physical (or, actual) diameters about and slightly less than 1 μm (Cichowicz 1983, Katz et al. 1980), however, the fewer particles present in the obscurant cloud with diameters greater than 1 μm may contain most of the mass of the suspended particulate matter. Aerosols observed in the field are polydisperse; they are made up of particles of many different diameters. The size distribution of such aerosols is often log-normal and may thus be well characterized by a mean or median size and a standard deviation.

Measuring the particle size distribution of an aerosol (the frequency of particle occurrence as a function of particle diameter) is important in describing an aerosol's physical characteristics. The particle size distribution of an aerosol may be based on particle number frequency, aerosol mass, or other parameters such as surface area or particle volume. The particle size distributions of the HC aerosols generated in this study were characterized by aerodynamic diameter rather than actual physical diameter. Determination of aerodynamic diameter provides information on the inertial characteristics of suspended particles. This method also accounts for the effects on particle transport caused by the shape of the individual particles that make up an aerosol without requiring actual characterization of particle shape.

The particle size distribution of HC aerosols was measured during most tests to provide information on particle size for comparison with transport and deposition measurements and to determine the influence aging, aerosol mass concentration, and environment (relative humidity) on particle size.

HC aerosols were sampled periodically during the tests using an Andersen ambient-style cascade impactor operated at approximately 28 Lpm. This device provided separation of the suspended particles in the HC aerosols into eight different aerodynamic size classifications ranging from approximately 0.5 to 10 μm. Samples were drawn from the wind tunnel 6 m downwind of the test section, an area of low wind speed. This allowed accurate sampling of the larger particles in the aerosols by reducing isokinetic sampling requirements, namely orifice velocity. Each stage of the impactor was covered with a preweighed, flat glass fiber substrate which was used to collect the depositing particulate mass. Substrates were weighed after each sample, and the particulate mass, along with the sampling flow rate, were

analyzed to provide particle statistics. After postsample weighing selected substrates were extracted with dilute nitric acid and chemically analyzed to provide information on the size distribution of inorganic constituents.

2.4.3 Aerosol Chemical Composition

In addition to characterization of the size distribution and mass concentration of HC aerosols generated in the wind tunnel, the chemical composition of the aerosols was measured. Measurements were performed on collected particulate mass from isokinetic filter samples, deposition coupons suspended in the air stream, cascade impactor samples, and other deposition coupons such as dry and wet plastic petri dishes located on the floor of the wind tunnel test section. Other samples were obtained during selected tests and included on-line gas chromatograph analysis for chlorocarbon compounds and liquid impingers for both organic and inorganic analyses. From these samples, and from samples of plant tissue and surface soil, the chemical composition of HC aerosols was determined for airborne particles and particles deposited to various surfaces.

Measurements of the water mass associated with the suspended particles in HC aerosols were performed to provide information regarding the influence of environment on the aqueous mass fraction of the aerosols. Aerosols generated and maintained in high humidity conditions (~90%) were anticipated to gain mass and increase in size; both phenomena probably increasing the effectiveness of the aerosol as an obscurant. The water fraction of HC aerosols was measured by comparing the fresh and desiccated mass of particulate matter on isokinetic filter samples. These data were used to provide the desiccated, or nonaqueous aerosol mass concentration, a second measure of aerosol mass concentration during the exposure tests (the first measure being fresh, or actual aerosol mass).

Samples of HC aerosols withdrawn from the wind tunnel were shown to come to equilibrium with the humidity in the laboratory after they were removed from the wind tunnel atmosphere. The procedure for measuring the relative percentage of collected particulate matter as free, or chemically unbound, water consisted of weighing samples immediately after collection. However, for cases when the relative humidity in the wind tunnel was not equal to that in the laboratory, a change in mass of the samples was possible that would reduce the sensitivity of the procedure. Samples obtained during the relative humdity test series provided the opportunity to check the measurement procedure. Particulate matter collected on isokinetic filter samples during tests HC-16, -17, and -18 was weighed periodically following collection, as shown in Figure 2.8. For these tests, relative humidities were controlled at 20, 55, and 85% within the wind tunnel, while the RH of laboratory atmosphere was 35, 38, and ~15%,

respectively. Samples from the test HC-16 actually gained mass during gravametric analyses because the laboratory humidity was greater than that in the wind tunnel.

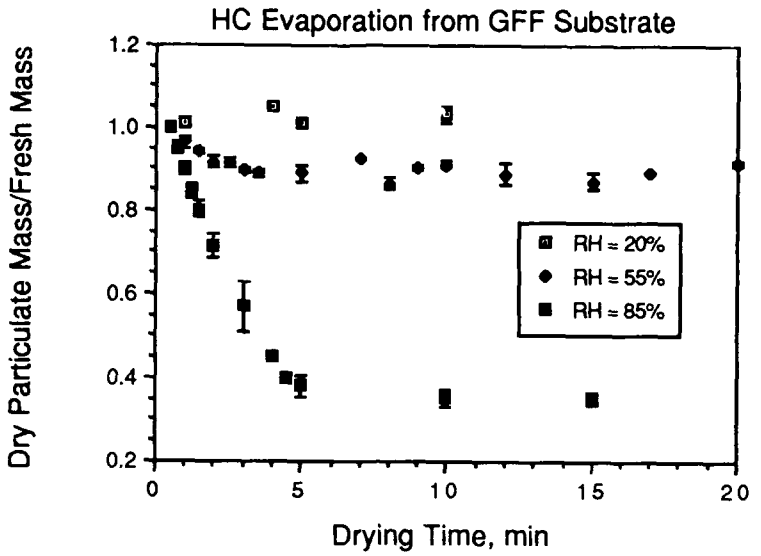


FIGURE 2.8. EVAPORATION OF VOLATILE FRACTION OF THE HC AEROSOL SAMPLES COLLECTED ON ISOKINETIC 25-mm GLASS FIBER FILTER SUBSTRATE (TESTS HC-16, -17, AND -18)

All samples revealed constant sample evaporation rates over the first 3 or 4 min of drying. Based on a linear extrapolation of these data to the time they were removed from the wind tunnel atmosphere, the original fresh, or actual, mass of the samples could be determined. Test HC-18 provided the worst-case condition; measurements of actual sample mass made at approximately 45 ± 15 s after removing the samples from the wind tunnel were seen to be approximately 3 to 6% less than the actual mass due to evaporation of water. Both other tests, at low and mid-range humidities indicated that measurements at 45 ± 15 s were within 3% of predicted sample mass. Because of the small magnitude of these potential errors in measurement, no correction factor was applied to the data.

The quantity of zinc mass collected on isokinetic filter samples was measured to provide a third type of aerosol concentration, the airborne mass concentration of zinc. This measure was performed because the quantity of particulate matter depositing to plant, soil, and other surfaces was generally determined by measurement of increased levels of zinc on the test subjects. Thus the measurement of zinc aerosol mass concentration provided a way to compare aerosol characteristics with aerosol mass loading and mass loading rates (deposition velocities) to exposed surfaces, and biological and chemical effects on test subjects.

Procedures for measurement and analysis of these and other samples for determination of the other chemical constituents of the HC aerosols are presented elsewhere in this report.

2.5 CHEMICAL CHARACTERIZATION OF HC SMOKE CONSTITUENTS

2.5.1 Organic Analyses

Wind Tunnel Gas Monitoring

The composition of the gas phase components released from the HC aerosol generation were monitored with an on-line gas chromatograph specifically designed and constructed for this task. The principal components of the system, schematicaly depicted in Figure 2.9, are the Hewlett/Packard (HP)-5890 GC fitted with an electron capture detector, an HP-3392 integrator for data acquisition and valve action control, and an HP-14905 external events module for solenoid control. Completing the gas sampling valve control system (not shown in Figure 2.9) are a Valco multiposition valve control module and a Valco stream selection module.

The gas sampling system uses two pneumatically controlled sampling valves, one to select the location from where the sample is taken, and a second to inject a measured volume of sampled gas into the gas chromatograph for subsequent separation and detection. The sampling valve action is controlled through time parameters programmed into the HP integrator. During the HC tests, the instrument was programmed to sequentially sample the aerosol generation chamber, the wind tunnel, the laboratory air surrounding the wind tunnel, and two calibration gases. After several initial experiments indicated that the chlorocarbons produced during fog generation were not leaking into the room air, the sampling was confined to the test section of the wind tunnel during experiments. The calibration gases and laboratory atmosphere were sampled before and after each test. Sampling of the aerosol generation chamber was suspended because the large amount of particulates associated with the dense aerosol were fouling the gas sampling lines.

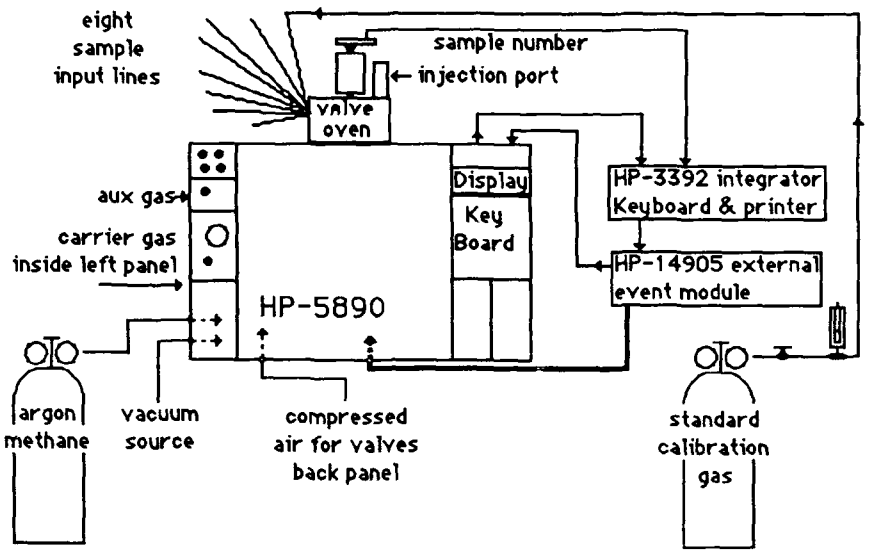


FIGURE 2.9. SCHEMATIC DIAGRAM OF ON-LINE GAS CHROMATOGRAPH USED FOR SAMPLING THE WIND TUNNEL ATMOSPHERE DURING HC EXPOSURE TESTS

The gas sampling valves were mounted on the gas chromatograph in an temperature-controlled insolated box heated to 150°C. The gas sampling valve injects a predetermined volume of gas from the selected gas stream into the analytical column. A diagram of the stream selection and stream sampling valve is given in Figure 2.10. Initially a 15-cm section of an HP-1, 0.53-mm-ID column coated with a 2.65-µm-thick methyl silicone gum was used for the sampling loop. The volume of this tube was 33 µL. Later, the fused silica loop was replaced with a stainless steel sampling loop with a volume of 13.75 µL. It was determined that the stainless steel loop was more resistant to surface adsorption and therefore responded more quickly to changes in sample streams.

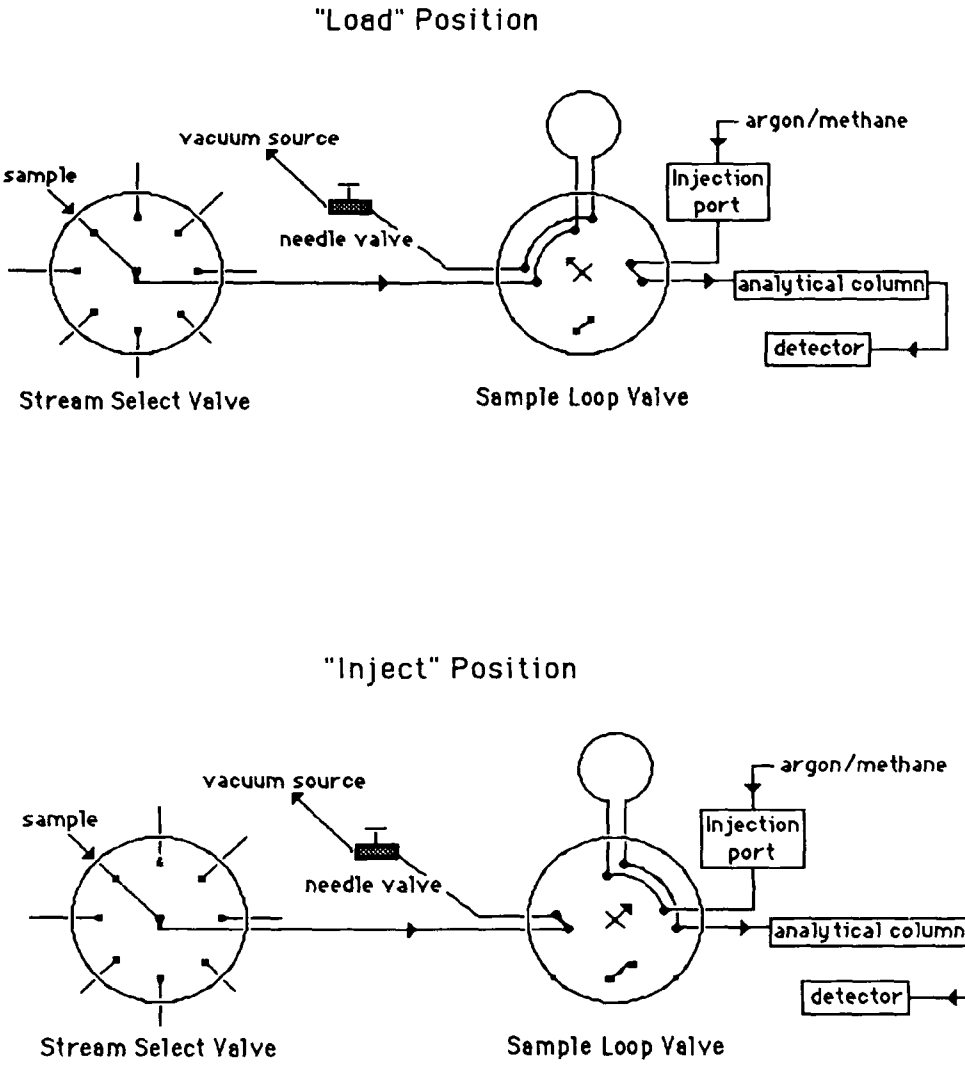


FIGURE 2.10. STREAM SELECTION AND STREAM SAMPLING VALVE CONFIGURATION FOR ON-LINE GC. (TOP) SAMPLING VALVE IS IN THE SAMPLE LOAD POSITION. (BOTTOM) SAMPLING VALVE IS IN THE SAMPLE INJECT POSITION. THIS IS ALSO THE NORMAL STANDBY POSITION

The sampling lines between the stream selection valve and the sampling location (wind tunnel test section and aerosol generation chamber) were 1/8-in. stainless steel tubing. The tubes were wrapped with heat tape, and a Variac was used to regulate the sampling line temperature to 150°C so that the sampled material would not condense in the lines before reaching the sample loop.

A 5-meter HP-1, 0.53-mm-ID column coated with a 2.65-µm-thick methyl silicone gum was used for the chromatographic seperation of the gas components. This column type and length seperated the four compounds of interest (carbon tetrachloride, tetrachloethene, hexachloroethane, and hexachlorobenzene) with sufficient speed and resolution. A 90:10 mixture of argon and methane was used for both the carrier gas and the support gas in the electron capture detector. During sample analysis, the column oven was held at 50°C for 2 min after sample injection and programmed to 150°C at a rate of 50°C/ min. Following this it was held at 150°C for 2 min and then returned to the initial temperature. The electron capture detector response was calibrated with external liquid and gas standards previous to the initiation of each set of experiments. The response of the detector to the different concentrations of the chlorocarbons were plotted against the quantity of material injected, and a regression line was fitted to that data. A typical plot used for detector calibration is shown in Figure 2.11. The regression equation was subsequently used to calculate the quantity of material injected with the gas sampling loop, and a concentration was calculated by dividing by the sample loop volume.

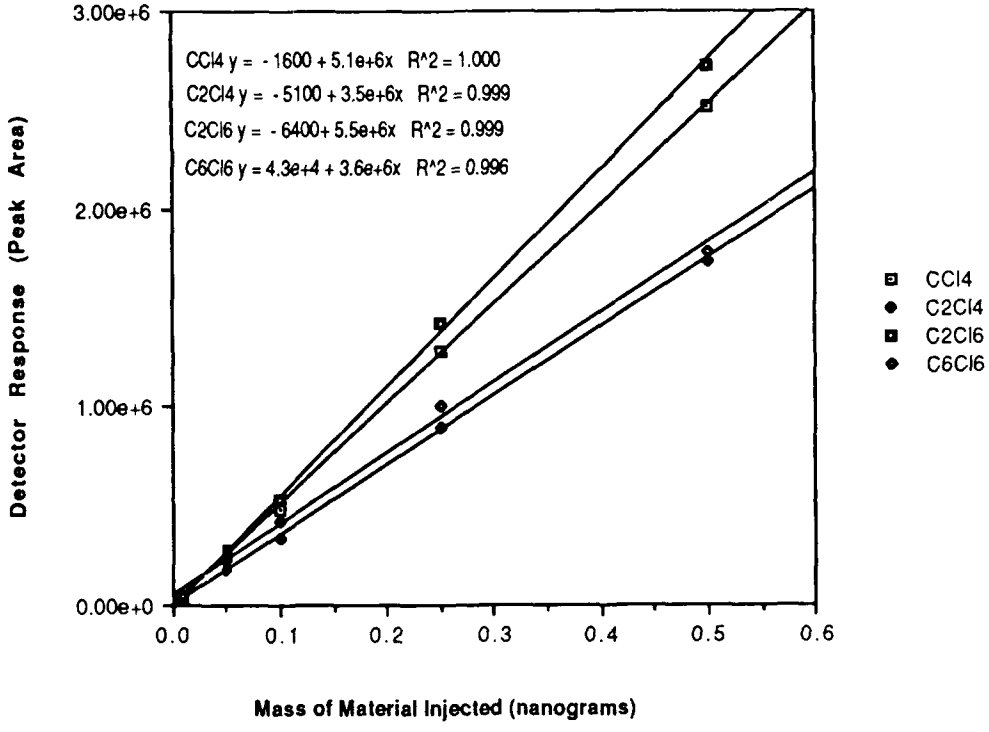


FIGURE 2.11. TYPICAL CALIBRATION PLOT FOR WIND TUNNEL GAS CHROMATOGRAPH

Aerosol Deposition Samples

Deposition coupons were exposed to the aerosol smoke as described in the previous section. Following exposure, the samples were collected with forceps, and placed directly into solvent-rinsed 20-mL glass vials containing 10 mL of distilled-in-glass hexane. The bottles were fitted with Teflon-lined screw caps and shaken for 1 min. After the samples had set for about 1 h they were stored at -80°C until analysis. For analysis, 1 mL of the deposition coupon extracts were transferred to auto sample vials. The instrumental conditions used for separation and quantification are described below.

Integrated Aerosol/Gas Samples

Chlorocarbons present in the gas /aerosol phase were collected during the HC smoke tests using blubbers containing 50 mL of hexane. The sampling procedures are described in Section 2.5.1. A set of bubblers were run during most HC generation experiments. Immediately following a test, the 50 mL of hexane used for sample collection was transferred to a amber glass bottle and fitted with a Teflon-lined screw cap. The samples were subsequently transferred to a -80°C freezer where they were stored until analysis.

Plant and Soil Sample Analysis

The analysis of plant foliage for organic residue was confined to the relative humidity test series. Five different species of plants, representative of the typical vegetation found on test ranges, were selected for exposure. These included bush bean, sagebrush, ponderosa pine, short-needle pine, and tall fescue. There were six replicates of each plant species, and two samples were collected from each plant to average the variation often found in the deposition of material through a plant canopy. Following the relative humidity tests, the plants were sampled immediately following their removal from the wind tunnel, and at 2, 4, and 9 days following exposure. The chlorocarbons were directly extracted from the plant leaf tissue into 10 mL of distilled-in-glass hexane (Burdick and Jackson, Muskeegon, Michigan). Immediately following extraction, the leaf tissue samples were blotted dry and their surface areas were measured.

Two different soils, the Burbank and the Maxey Flats soils, were also exposed to the HC smoke. A more complete description of these soils is provided below. Petri dishes filled to a depth of about 1.5 cm with the soils were randomly placed in the wind tunnel during exposure. Immediately following exposure and at 2, 4, and 9 days postexposure the soil was sampled using a solvent-rinsed cork bore. The chlorocarbons were extracted from the soil into 10 mL of hexane.

Instrumental Conditions

All hexane extracts were analyzed by gas chromatography using an electron capture detector. The samples analyzed included the bubbler solutions, the deposition coupon extracts, and the plant and soil extracts. Two gas chromatographs were used for the sample analysis, a HP5840 and a HP5880. Both GCs were fitted with the HP7672 autosamplers. Initially a 30-m x 0.25-mm-I.D. J and W DB-5 bonded phase column was used for the chlorocarbon analysis. A J and W DB-624 of the same dimensions was later substituted for the DB-5 because the DB-624 provided baseline resolution of CCl4 from other chloromethanes. This allowed for a more accurate integration of peak areas. Helium was used as the carrier gas for all analyses. The injection ports were operated at 260°C and the electron capture detectors at 300°C. The compounds were eluted under the following temperature program: initial temperature 40°C/hold 4 min, ramp to 214°C at 6°C/min, then ramp to 280°C at 20°C/min. The detector response for each instrument was calibrated using external standards as described in the section on the wind tunnel GC. A full set of calibration standards was run before each group of 30 samples. This established the calibration intervals at every 38 h.

2.5.2 Inorganic Analyses

Deposition velocities were measured to plant, soil, and surrogate surfaces located within the wind tunnel test section during HC tests. Sampling collection methods for inorganic analysis of HC aerosols included aerosol mass filters, Andersen cascade impactors, static deposition filters and wet and dry surfaces, and aqueous bubbler samplers. Surrogate deposition coupons were used to provide relatively uniform surfaces for aerosol deposition for comparison with plant and soil deposition data.

Deposited aerosol mass was measured gravimetrically following each test as noted. In addition, coupons were divided into sets for zinc and for chlorocarbon analysis, by acidic and organic leaching, respectively. Static deposition filters used were 47-mm glass fiber filters. One set of deposition coupons included six 47-mm glass fiber filters suspended horizontally in the center of the test section. These filters provided a plane surface parallel to the direction of the approach flow. Some of the filters did, however, tilt into the wind during the 4.5-m/s tests (HC-9 and HC-14). Analysis of glass fiber filter samples and blanks for zinc revealed that the background zinc levels possibly affected the procedure. Further measurements indicated a highly variable zinc content that very roughly approximated one-tenth of the zinc collected from the aerosol in early studies. To reduce this potential source of error, glass fiber filters for air sampling and deposition velocity measurements were soaked in 2 M acid (HCl; later HNO_3) and multiple baths of deionized water, followed by freeze-drying to minimize physical damage, prior to use. Following weight determinations, both exposed filter types were leached in acid

(0.25 M HCl in early studies, with selected filters leached in deionized water for comparison; 0.01 M HNO_3 in later studies) for determination of Zn and trace metals. Leachates were filtered through prerinsed Millex® 0.2-μm GVWP (Millipore) syringe filter units. Selected nitric acid leachates were also analyzed for Cl^-, as described below. Static deposition onto wet and dry surfaces was monitored using glass (in early studies) and polystyrene petri plates containing deionized water or dry, respectively; dry plates were leached post exposure with water or acid solutions for chemical analysis, but were not weighed for direct deposition mass determination.

Bubbler samples consisting of 50 mL deionized water were taken at a target flow rate of 96 mL/min for 14 to 20 min. A buildup of film, presumably elemental carbon and organics, was observed on all aqueous extracts of the various surfaces, but caused minimal problem with inorganic component analyses, once filtered.

Routine dose quantitation parameters including those for filter coupons, impactor stages, and plant and soil samples were based on the major inorganic constituent, Zn. All analyses for aerosol metal constituent determinations were done by Jarrell Ash Model 750 Inductively Coupled Argon Plasma emission spectrometry (ICAP) on the leachate solutions. Attempts to utilize a chromatographic separation technique for separation and detection of Zn based on Sevenich and Fritz (1983) generally failed due to the high concentrations of organic constituents in the HC smokes.

Chloride analysis by ion chromatography (IC) was performed on water extracts of filters and deposition surfaces using AS1 or AS3 (Dionex) columns and standard eluent of 3 mM $NaHCO_3$ + 2.4 m M Na_2CO_3, or AS4A (Dionex) columns and eluent of 1.85 mM Na_2CO_3 + 1.75 mM $NaHCO_3$. Limited Cl- analyses were also performed by IC on acidic extracts (0.01 M HNO_3) of filter or deposition surfaces using normal AS1 (Dionex) columns. Dionex IC models 10 or 16 with conductimetric detection were used throughout.

2.5.3 Analysis of Chemical Effects on Diverse Soils

A primary goal in these test series was to observe the effects on soils covering a wide range in soil properties such as might be found under actual field conditions. Therefore, emphasis was placed on the diversity on soils rather than on the statistical response of a single soil to the aerosol stress. Accordingly, six different soils covering a wide range of properties (Table 2.5) were exposed to the HC aerosol. These determinations were made on aliquots

TABLE 2.5. SELECTED SOIL AND PROPERTIES OF SOILS USED IN THE HC EXPOSURE TESTS

Property	Burbank	Maxey Flats	Ritzville	Yamac	Shawano	Quillayute	Palouse
Description	Silt Loam	Silt Loam	Loam	Clay Loam	Loam	Silt Loam	Silt Loam
pH (100% field capacity 0)	7.4	4.4	6.2	8.4	4.8	4.7	5.6
Org.C (%)	0.52	2.2	0.70	0.74	13.7	12.9	1.86
Sulfur (%)	0.053	nd	0.54	0.025	0.084	0.124	0.043
Nitrogen (%)	0.061	0.22	0.09	0.095	0.67	0.89	0.16
Total P (µg/g)	2400	nd(a)	1420	720	1440	3900	3770
PO_4^{3-}-P (µg/g)	4.8	2.4	nd	6.7	7.6	0.13	5.8
Sand (%)	45.1	20.6	43.6	26.2	45.3	10.0	1.1
Silt (%)	51.4	65.4	43.9	46.4	40.0	63.0	77.5
Clay (%)	4.0	14.2	12.5	33.4	14.7	27.0	21.4
Ash(%)	98.0	nd	96.9	96.5	83.8	70.2	93.8
Carbonae/ bicarb.(%)	<0.5	<0.1	<0.5	4.65	<0.5	<0.5	<0.5
Ammonia-N (µg/g)	6.1	63	9	99	45	36	18.3
CEC (meq/100 g)	5.5	12.6	28.0	45.1	nd	nd	23.8

(a) Not determined.

from soils collected at benchmark soils which were used for the thin lens soil exposures, but were not the same batch as the soils actually used for planting studies. Palouse, typical of eastern Washington agricultural soils, is included in the table because it was utilized in later microbial studies, but it was not exposed as a thin soil lens. Two of the soils, Burbank and Maxey Flats, are those used for growing the plants for exposure. Burbank is a well-characterized alkaline silt-sand that readily supports the growth of grass species. Maxey Flats is a silt-clay noncultivated soil that has low nutrient status; it will support marginal growth of grass species, but has not been well characterized. Burbank and the remaining four soils were selected from the library of characterized soils we currently maintain. Air-dried aliquots (10 g) were spread evenly on polystyrene petri dish covers (165.1 cm^2) having 0.8-cm sides (the lower the side-to-surface area ratio, the lesser the turbulence created by the wall). Two of these soils, Burbank and Maxey Flats, were exposed during all relative humidity runs, while the other four soils were exposed during the midrange humidity test.

Thin soil coupons were exposed to HC aerosols as air-dried aliquots (sieved <40 mesh) spread evenly over polystyrene petri plates at a rate of 0.065 g/cm^2. Following exposure, the soils were extracted with deionized water (10:1 water to soil ratio) under

controlled conditions (~ 25°C, 60 rpm, aerobically in the dark) for up to 15 days. One additional set of six soils was held for 2 days following exposure before being contacted with water and incubated. All soils were sampled at 1 and 5 days of incubation. In addition, one set of six soils plus controls were sampled at 2, 9, and 15 days following initial water contact. Since an acidity effect was possible, following an initial 5-day incubation of a set of six control soils, HCl was added (1 mL of 0.1 M HCl) to approximate the pH change observed in the exposed soils (due either to HCl or $ZnCl_2$), and these soils were studied at 5 and 10 days additional incubation. During the rainout test (HC-19), it was more difficult to control thin-coupon soils since the rain and plant runoff volume exceeded the normally added volume of water in most locations in the exposure section. Therefore, duplicate samples of Burbank and Maxey Flats soils were exposed upwind of the rainout section; aliquots of Burbank and Maxey Flats soils were then placed in deeper collection dishes within the rainout area. The variance in water volumes collected was a result of both the variation in droplet distribution and accumulated runoff from some of the exposed plants in close proximity to the soil coupons. As an added comparison, 100 mL of collected rainout water was also used to contact an unexposed 10-g aliquot of Burbank soil.

Because control soils were treated in like manner to exposed soils, no attempt was made to control evaporation through the foam- or cotton-plugged incubation flasks. Evaporation rate was estimated at 0.39 ± 0.02 g/day (N=2) for 10 g/100 mL contacts, and 0.53 ± 0.04 g/day (N=12) for 20 g/200 mL contacts.

At each sampling interval, a 6-mL aliquot of each soil solution was withdrawn with a plastic syringe and filtered [0.22-μm Millex GVWP unit (Millepore), prerinsed with 10 mL deionized water], discarding the first 0.5 mL of effluent. Aliquots were taken for major elemental analysis (by ICAP), anions (by IC), organic and inorganic carbon (by Dohrmann DC-80 Carbon Analyzer), and pH (by Orion Ross electrode and Orion Model 611 pH meter). Selected samples were also analyzed by Ion Specific Electrodes (ISE) for fluoride (Orion Model 9606 combination electrode) and ammonia (Orion Model 9512 gas-sensing membrane electrode).

2.6 PLANT AND SOIL SELECTION AND CULTIVATION

2.6.1 Plant Selection and Cultivation

The native species including sagebrush, ponderosa pine, and short-needle pine are found associated with different training environments throughout the United States or used in revegetation, while bush bean (used as a sensitive indicator species for soft crops), the pines and grass are important agronomic species found adjacent to many training installations.

Plant sources and characteristics are as follows:

- Big Sagebrush (Artemisa tridentata, vaseyana). A medium-sized, perennial shrub found over vast expanses of the arid and semiarid western states. It grows in relatively harsh environments on alkaline soils and at elevations from sea level to 7000 ft. Source: Native Plants Inc., Sandy, Utah. Age: 2-year-old seedlings.

- Ponderosa Pine (Pinus ponderosa). A large coniferous forest species common to western North America. It grows at a range of elevations and is relatively tolerant to drought. It requires moderate soil fertility. Source: MacHugh Nursery, Eltopia, Washington. Age: 2-year-old seedlings.

- Short-Needle Pine (Pinus echinata). A coniferous tree species indigenous to the southeastern United States. This variety is used extensively in reforestation. Source: J.P. Rhody Nursery, Gilbertsville, Kentucky. Age: 2-year-old seedlings.

- Tall Fescue (Festcua elator). A perennial, cool-season bunchgrass that grows well on dry or wet, alkaline or acid soils. A rather ubiquitous range. Source: Native Plants, Sandy, Utah. Grown from seed.

- Bushbean (Phaseolus vulgaris, tendergreen). An agronomic species that is relatively sensitive to chemical insults, based on prior experience. Grown from seed.

These five plant species provided a range of canopy type, cuticular structure, and thickness and were suitable for evaluating phytotoxic response to obscurant smokes and for evaluating deposition velocity under a range of environmental conditions. Ponderosa pine, short needle pine, and sagebrush were maintained in the greenhouse before use. These species were allowed to go dormant in the fall of the year; in December, the greenhouse temperature was increased and photoperiod was artificially adjusted to break dormancy. Before their experimental use in the spring, groups of these plants were transferred to growth chambers and allowed to equilibrate for 30 days, where they were maintained at day/night temperatures of 32°C/21°C, a 16-h photoperiod (approximately 500 mE m^{-2} sec^{-1}, PAR, at leaf surface), and 50% relative humidity. Bushbean was planted and grown in growth chambers under the same conditions. Tall fescue was grown from seed and maintained at day/night temperatures of 27°/15°C, a 10-h photoperiod (approximately 500 mE m^{-2} sec^{-1}, PAR, at leaf surface), and 50% relative humidity.

Both pine species were grown on a commercially available loam soil, while the

Both pine species were grown on a commercially available loam soil, while the sagebrush, tall fescue, and bushbean were grown on Burbank silt-sand. The latter were used to evaluate direct foliar contact toxicity, and at no time was the soil of these test systems exposed to HC smokes.

2.6.2 Soil Selection and Characteristics

Two soils were used to evaluate indirect soil/plant effects. For this evaluation, soils were contaminated with fog oil smokes prior to the seeding and growth of the grass species. The two soils used were Burbank (found at Hanford, Washington), an alkaline silt-sand that readily supports the growth of the grass species; and Maxey Flats (found at Morehead, Kentucky), a silt-clay that is noncultivated, has low nutrient status, and will support marginal growth of the grass species. All soils were maintained at 50% to 66% of field capacity before and after experimental use. Their physical and chemical characteristics of the Burbank and Maxey Flats soils employed in the soil/plant studies are provided in Table 2.5.

2.7 PLANT/SOIL MEASUREMENTS

2.7.1 Foliar Contact Toxicity Responses

In evaluating direct foliar contact toxicity, plant canopies were exposed to smokes under a range of concentration, time, and atmospheric conditions. In all cases, soils were isolated from canopies by bagging the soil containers at the lower plant stem to preclude any indirect effects arising from soil contamination. All foliar exposures were conducted in the illuminated portion of the wind tunnel test section.

Toxicity responses arising from direct contact of smokes with foliar surfaces, namely those that are readily visualized or phenotypic, were evaluated using a modified Daubenmire Rating Scale (Table 2.6). This nonparametric approach provides for a rapid comparison of gross toxicity, and its relative intensity with time of postexposure. In addition, grasses that are harvested 3 to 4 weeks after exposure (direct canopy effects) were permitted to regrow through one or more subsequent harvests, and dry matter production was monitored. Regrowth and monitoring allows for evaluation of any residual plant effects resulting from foliar absorption and root accumulation of smoke components.

TABLE 2.6. CODING FOR MODIFIED DAUBENMIRE RATING SCALE AND ASSOCIATED PHYTOTOXICITY SYMPTOMS

Symptom/Intensity	Description
Modified Daubenmire Rating Scale	
0	no obvious effects over controls
1	5% of plant foliage affected
2	5% to 25% of foliage affected
3	25% to 50% of foliage affected
4	50% to 75% of foliage affected
5	75% to 95% of foliage affected
6	95% to100% of foliage affected
Phenotypic Responses	
OGA	old growth affected
NGA	new growth affected
O&NGA	old and new growth affected
TB	tip or leaf edge burn
LBD	leaf burn and leaf drop
NS	necrotic spotting
LD	leaf abscission or needle drop
Chl	chlorosis
BD	blade dieback
LC	leaf curl
W	wilting
GD	growing tip dieback
D	plant dead
F/SA	floral or seed/fruit abortion
(value)	indicates the length in centimeters that needles or leaves exhibit dieback or burn

2.7.2 Photosynthetic Measurements

Oxygen Electrode (Polarographic) Measurements. Leaf samples were taken prior to, immediately following, and at several intervals after exposure for analysis of oxygen evolution and uptake. Leaves were excised from the plants, placed in moistened paper towels, and maintained on ice at approximately 4°C until assayed. They were then wetted with distilled water and sliced with a razor blade into pieces <5 mm in length or diameter. The pieces were transferred to an assay medium consisting of 2 mM $CaCl_2$, 10 mM sodium bicarbonate, and 20 mM N-2-Hydroxyethylpiperazine-N'-2-ethansulfonic acid (HEPES), pH 7.6. Paired tissue samples were taken from this solution and placed directly into paired, water-jacketed (3.9 ml of control media at 20±1°C) cuvettes. The suspension was continually stirred with magnetic stirrers. The cuvettes were then covered with aluminum foil for dark respiration for approximately 25 min, until a steady-state rate was obtained. They were then illuminated with saturating light (>1200 μEinsteins $m^{-2}s^{-1}$) at 600 nm for an additional 20 min to obtain a steady-state rate of photosynthesis. After illumination, the tissues were removed from the

steady-state rate of photosynthesis. After illumination, the tissues were removed from the cuvettes, and blotted and dried overnight in a 75°C oven so the dry weight could be obtained. Assays were run in triplicate and the data expressed as micromoles of O_2 $h^{-1}g$ dry wt^{-1}.

Infrared Gas Analyzer (IRGA) Measurements. The exchange of CO_2 from the plants may be measured by the use of an Infrared Gas Analyzer (IRGA). A gas analysis system was constructed in the wind tunnel; a simplified schematic of its components is given in Figure 2.12.

A Beckman Model 865 IRGA in the differential configuration was employed to measure differences in CO_2 concentration (μL/L) in air that had passed through the plant chamber versus that of the original filtered outside air (see Figure 2.8). The cylindrical Plexiglass® plant chamber (45 L/cm^3) was placed in the same large growth chamber in which the plants were maintained during the exposure series to minimize environmental differences. Plant chamber temperature was maintained within ±1°C of the growth chamber. Light intensity at canopy level in the plant chamber was ~95% that of the growth chamber (400 μE $m^{-2}s^{-1}$). Flow rates (10 Lpm) and backpressures were used to calculate rates of Net Carbon Exchange (NCE) (μmol CO_2/s/plant). Measurements of individual plants were taken prior to exposure and at various times during the experiment. In addition, control plants not exposed to HC smoke were also measured intermittently over this period, to provide a point of reference.

2.7.3 Indirect Plant Effects

Indirect plant effects were evaluated by exposing Burbank and Maxey Flats soils to smoke aerosols. These soils (444 and 526 g dry weight of Maxey Flats and Burbank, respectively) were brought to moisture level, placed into 4.5-in.-diameter by 4-in.-high pots, the surface leveled, and pots exposed to smokes. Four days after being exposed, the soils were seeded with 15 tall fescue seeds. This approach resulted in contamination of only the soil surface; postplanting irrigation should result in some redistribution of smoke components down the soil profile. Indirect plant effects resulting from smoke contaminants deposited to soils were determined by evaluating percentage of germination and dry matter production using blando brome as a test species. Dry matter production for plants grown on contaminated soils was followed through two or more harvests.

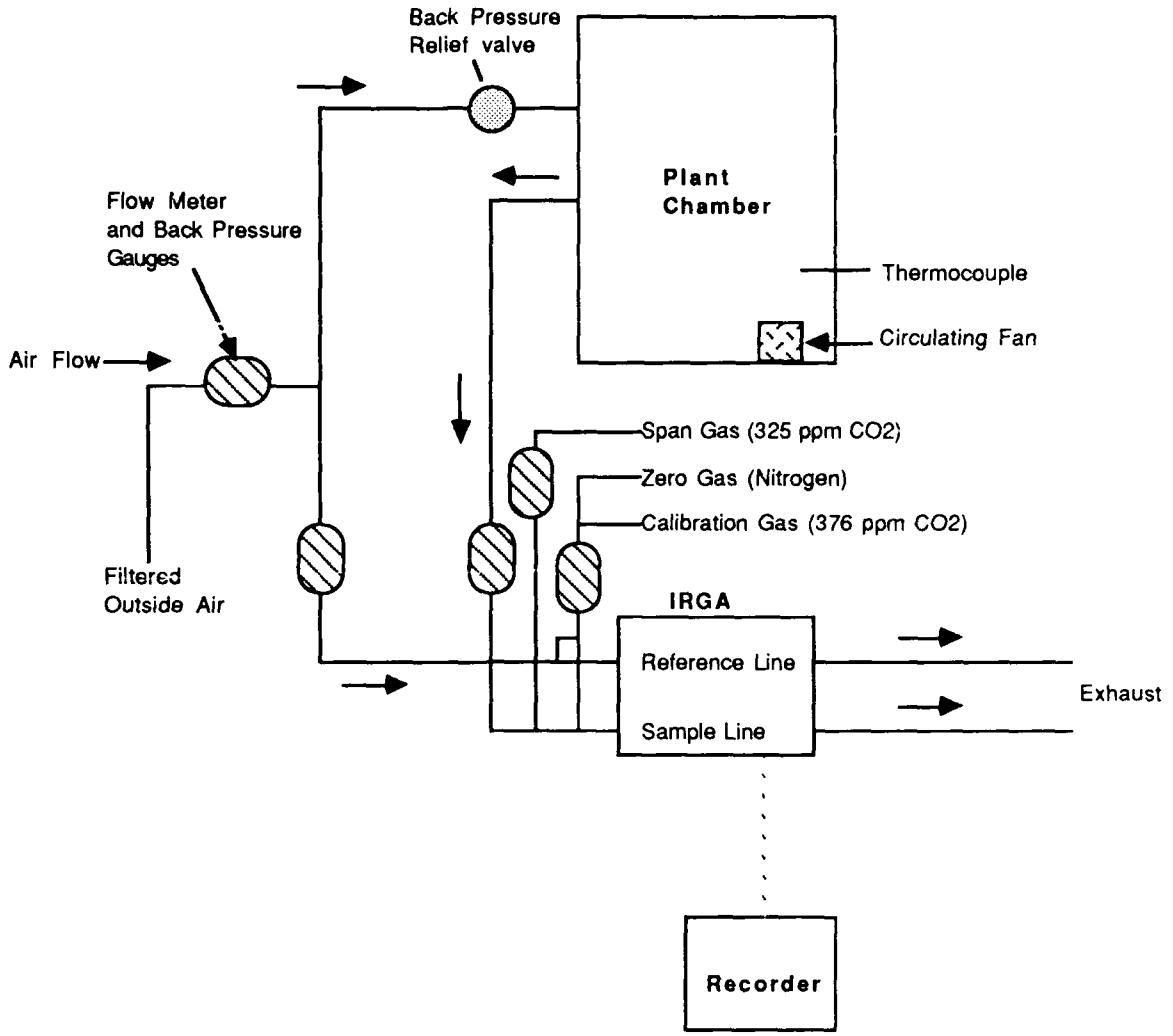


FIGURE 2.12. SCHEMATIC DIAGRAM OF GAS EXCHANGE SYSTEM USED IN MAKING NET PHOTOSYNTHETIC AND DARK RESPIRATION MEASUREMENTS

2.7.4 Quantitation of Exposure/Dose

The evaluation of plant toxicity responses to airborne contaminants requires a basis for intercomparison of treatments and variables. In all of the toxicity studies, the point of reference is the mass loading value or exposure dose, as opposed to air concentration or exposure duration, to provide a specific dose value for each plant. The mass loading rate is determined by chemical measurement of the amount of smoke deposited to a unit area or weight of foliage, and is an absolute index of dose. In the case of HC smokes, total Zn associated with foliar surfaces was employed, minus the Zn extracted from control tissues. Mass loading to soils

was estimated based on loading to filter coupons, dry petri dishes, and wet petri dishes followed by extraction as noted earlier. Quantitation of interception efficiency based on type of receptor surface (namely the type of canopy structure) is based on computed deposition velocities. The velocities are calculated from the air concentration, exposure duration, and the quantity of smoke (hydrocarbons) deposited per unit surface area.

The rates at which aerosols are deposited to the plant and soil surfaces in the wind tunnel, or the deposition velocities, were determined as functions of the Zn mass concentration of the aerosols, mass deposited, and exposure duration. Deposition velocity results were compared for exposure variables including duration, relative humidity, and wind speed.

2.7.5 Post-Exposure Simulated Rainfall

The intensity of phytotoxic responses to foliar contaminants can be modified by the presence or absence of surface moisture. Immediately following exposure, subsets of exposed plants were subjected to a simulated rainfall (Figure 2.13) equivalent to 1.0 cm, as described in Cataldo et al. (1981). Simulated rainfall permitted evaluation of either the ameliorating effects of foliar surface wash-off, or any intensification of effects resulting from the presence of surface moisture and increased foliar uptake.

2.8 SOIL MICROBIOLOGICAL MEASUREMENTS

Two soils were used to evaluate the microbiological effects of hexachloroethane (HC) smoke exposure. They were Burbank (sandy, skeletal, mixed, xeric, Torriorthent) sandy loam soil found at Hanford area of Washington and Palouse (fine-silty, mixed, mesic, Pachic Ultic Haploxerolls) silt loam soil typical of eastern Washington agricultural areas. Their physical and chemical characteristics are listed in Table 2.5.

FIGURE 2.13. POST-EXPOSURE SIMULATED RAINFALL SYSTEM

Large petri dishes (150 X 15 mm) containing 50 g of air-dried Burbank or Palouse soil were moistened with 10 ml of distilled water. For the range-finding test (RFT) series, the soils were exposed to HC obscurant smoke for 1, 2, 3 and 4 h (HC-6, HC-7, HC-4, and HC-5, respectively) at a relative humidity of 40 to 45% and at a wind speed of 0.9 m/s (2 mph) in the PNL Toxic Aerosol Test Facility according to the described test protocol. Concentrations of HC at these exposures ranged from 380 to 480 mg/m^3. For the relative humidity (RH) test series, soil was exposed to HC smoke for 4 h at relative humidities of 20, 55, and 85% (HC-16, HC-17, and HC-18, respectively) and at a wind speed of 0.9 m/s (2 mph). Concentrations of HC at these exposures ranged from 470 to 1140 mg/m^3. For the cumulative dose (CD) test, soil was exposed nine times of 3 h each for a total exposure time of 27 h at a relative humidity of 52% to 60% and at a wind speed of 0.9 m/s (2 mph) over a period of 18 days (HC-22b through HC-30b). Mass concentrations of HC smoke ranged from 634 to 753 mg/m^3 during these exposures. Soil moisture lost during each exposure was measured by weight loss and replaced by adding deionized water immediately after each exposure. Average moisture loss was about 15% after each exposure. Table 2.7 summarizes the exposure conditions and aerosol characteristics for these tests.

Soil respiration of the Palouse soil was measured with an electrolytic respirometer incubation system described by Knapp et al. (1983). After the exposure, the smoked and control Palouse soils were transfered to pint-size screw cap bottles. Control and exposed soil received 2 mL of distilled water while another control soil received 2 mLof 75 mg/mL glucose solution. Oxygen consumption by the soil was measured manometrically with the electrolytic respirometers at a controlled temperature of 20°C. Respiration was measured periodically for up to 2 weeks. Each treatment was replicated twice.

Soil dehydrogenase activity was assayed by a modification of the method of Tabatabai (1982). Aliquots of soil (1.5 g wet weight) were first mixed with 0.015 g of $CaCO_3$, 0.3 mL of 1% glucose or casamino acids, and 0.25 mL of the substrate, 2,3,5-triphenyltetrazolium chloride (3% w/v). After incubation at 22°C for 24 h, 10 mL of methanol was added to the soil to extract the product, 2,3,5-triphenylformazan (TPF). The solution was mixed thoroughly, centrifuged, and the absorbance of the supernatant determined at 485 nm. Soil dehydrogenase activity, expressed as micrograms of TPF produced per gram of dry soil per 24 h, was determined by comparing absorbance values to a standard curve prepared with reagent grade TPF and methanol.

TABLE 2.7. CHARACTERISTICS FOR HC SMOKE TESTS EMPLOYED IN THE STUDY OF MICROBIOLOGICAL EFFECTS

Test No.	Date	Temp. (°C)	Wind Speed (m/s)	Exposure Time (h)	Relative Humidity (%)	Aerosol Mass Concentration (mg/m^3)
HC-4 (RF)	6/25/86	23	0.9	3	~40	380
HC-5 (RF)	6/26/86	22	0.9	4	~45	450
HC-6 (RF)	6/26/86	22	0.9	1	~45	410
HC-7 (RF)	6/26/86	22	0.9	2	~45	480
HC-16(RH)	11/3/86	23	0.9	4	20	470
HC-17(RH)	11/5/86	23	0.9	4	55	610
HC-18(RH)	11/11/86	22	0.9	4	85	1140
HC-22b- 30b (CD)	2/9 to 2/27/87	21-23	0.9	3 each total of 27 h	52-60	634 to 753 each run

Soil phosphatase activity was assayed by the procedure of Tabatabai and Bremner (1969), as modified by Klein et al. (1979). One gram of soil was placed in 15-mL centrifuge tubes with 4 mL of modified universal buffer (MUB), which consisted of tris(hydroxymethyl)amino methane, 3.025 g; maleic acid, 2.9 g; citric acid, 3.5 g; boric acid, 1.57 g; 1 M NaOH, 122 mL; in 250 mL final volume. pH 8.65. One millileter of p-nitrophenol phosphate (0.025 M prepared with MUB buffer) was added to each tube. The tubes were stoppered, vortexed, and incubated for 1 h at 37°C. One millileter of 0.5 M $CaCl_2$ and 4 mL of 0.5 M NaOH were added to the tubes. The mixtures were centrifuged at 12,000 g for 10 min and absorbance of supernatant was determined at 400 nm. Phosphatase activity, expressed as micrograms of p-nitrophenol produced per gram of soil per hour, was determined by comparing absorbance values to a standard curve prepared with reagent grade p-nitrophenol.

All dehydrogenase and phosphatase activities were measured in triplicate and mean values compared with that of the control (unexposed) soil and expressed as a percent of the control.

Soil-nitrifying bacteria were enumerated by the microtechnique for most-probable-number analysis (Rowe et al. 1977) using media described by Alexander and Clark (1965). Ammonium-calcium carbonate medium for *Nitrosomonas* consisted of

$(NH_4)_2SO_4$, 0.5 g; K_2HPO_4, 1.0 g; $FeSO_4 \cdot 7H_2O$, 0.03 g; NaCl, 0.3 g; $MgSO_4 \cdot 7H_2O$, 0.3 g; and $CaCO_3$, 7.5 g in 1000 ml distilled water. Nitrite-calcium carbonate medium for *Nitrobacter* consisted of KNO_2, 0.006 g; K_2HPO_4, 1.0 g; $FeSO_4 \cdot 7H_2O$, 0.03 g; NaCl, 0.3 g; $MgSO_4 \cdot 7H_2O$, 0.1 g; $CaCl_2$, 0.3 g; and $CaCO_3$, 1.0 g in 1000 ml distilled water. The media were autoclaved at 15 lb pressure for 30 min. Aliquots (0.2 ml) were transfered to 25 wells of a sterile microplate. A tenfold serial dilution of soil was prepared with sterile 0.85% saline solution. Five wells were inoculated with 0.1 ml of 10^{-2} through 10^{-6} dilutions with five replicates at each dilution. After incubation for 6 weeks at room temperature in the dark, wells containing ammonium-calcium carbonate medium for *Nitrosomonas* were tested for the presence of nitrite and/or nitrate using the modified Griess-Illosvay and nitrate spot test reagents described by Schmidt and Belser (1982). Positive tests for nitrite/nitrate in these tubes indicate the presence of *Nitrosomonas*. Wells containing nitrite-calcium carbonate medium were tested for nitrite. A negative test for nitrite indicated the presence of *Nitrobacter*. Populations of both groups of nitrifying bacteria were calculated using a most-probable-number (MPN) table (Alexander 1982) and presented as the $\log_{10}$ of MPN per gram of dry soil.

2.9 SOIL INVERTEBRATE ASSAY

An earthworm (*Eisenia fetida*) bioassay system was used to elucidate the toxicity of the HC smoke constituents. An artificial soil containing 350 g sand, 100 g kaolin, and 50 g dried peat moss (adjusted to pH 6.5 with $CaCO_3$), was employed both for culture and for the earthworm exposures. Worms were fed twice weekly with fermented alfalfa, and soil moisture adjusted to 35% of dry weight. Exposure tests used 80 g of the artificial soil (placed in 100 x 25 mm petri plates), containing five mature worms. Three replicate plates were used for each test series as noted in the text. The tests were terminated after 14 days, and effects observed over this period. Effects scored included earthworm mortality and simple response to physical stimulus (touching). Mass loading or dose was determined on similar soil plates without worms.

3.0 RESULTS AND DISCUSSION

Hexachloroethane (HC) represents an important obscurant smoke in the Army's inventory, along with fog oil, and red and white phosphorus. Continued use of these smokes at both U.S. and foreign installations, particularly for training purpose and countermeasures development, requires that their potential impacts to the environs in which they are employed be understood.

In the following studies, an environmental wind tunnel was employed to control the critical smoke generation step and associated atmospheric parameters (temperature, relative humidity and wind speed), and thus simulate different environmental conditions under which plant and soil systems would be exposed. By measuring the chemical and physical characteristics of generated aerosols, the influence of dose rather than exposure concentration can be used as a basis for comparing any adverse environmental impacts. For assessment of impacts, several plant species are employed; these would be representative of plant species associated with many of the U.S. training installations. impacts are assessed based on direct contact toxicity, and indirect and residual effects of smoke-associated contaminants on growth. Impacts to soils are assessed by evaluation of key microbial processes, and earthworm bioassays.

3.1 SMOKE (AEROSOL) CHARACTERIZATION

Hexachloroethane (HC) aerosols were characterized during each test to provide information on concentration, particle size distribution, and aerosol chemical composition. These data were then used to establish dosing conditions, and employed as a basis of comparison of ecological effects to environmental components studied. Deposition velocities (V_d) were determined for HC aerosols to surrogate surfaces (Gelman glass fiber filters) suspended horizontally in the air flow to provide comparison with V_d values for horizontally oriented leaves, and loading rates to other test surfaces such as soil.

3.1.1 Aerosol Mass Concentration

The mass concentration of HC aerosols was measured at short intervals throughout each test to provide information on average dose and particle deposition velocity. Three primary types of aerosol mass concentrations were measured. The fresh aerosol mass concentration, or the total mass of all material associated with the smoke particles, was measured because it is the concentration most closely related to the relative obscurance of HC aerosols. This is based on the dependence of electromagnetic transmission on particle size and index of refraction. To provide information on the mass fraction of water associated

with the suspended particles, the desiccated aerosol mass concentration was measured by drying isokinetic aerosol samples. This information was compared to test environment (relative humidity) to provide a measure of aerosol evolution between generation and deposition. The third primary measure of concentration, the mass concentration of zinc in the wind tunnel, was determined by chemical analysis of isokinetic filter samples, and was performed to permit comparison of aerosol mass concentration with the amount of zinc deposited to test subjects. Such a comparison was required because the aerosol mass loading to plant and soil surfaces was determined chemically as mass of zinc per area.

The mass concentration of HC aerosols was held constant during each test, and ranged from 130 mg/m^3 to 1300 mg/m^3 throughout the entire HC test series. A summary of average aerosol mass concentrations for each test series is shown in Table 3.1 and Figure 3.1. Target aerosol mass concentrations were achieved by controlling the period of ignition of HC pots and by using pots with charges ranging from about 10 to 40 g. Periods of increasing and decreasing aerosol mass concentration corresponded to the aerosol generation events. Actual HC aerosol mass concentration histories during selected tests are shown in Figures 3.2 through 3.6. In the figures, the lines represent the actual aerosol mass concentration as measured by the laser transmissometer, and the discrete points indicate calibration data obtained from isokinetic filter samples.

TABLE 3.1. AVERAGE AND RANGE OF AEROSOL MASS CONCENTRATIONS DURING EACH SERIES OF HC OBSCURANT TESTS IN THE WIND TUNNEL

Test Series	Avg. Aerosol Mass Concentration		
	Actual (mg/m^3)	Desic. (mg/m^3)	Zinc (mg/m^3)
Range-Finding	480. ± 48	420. ± 44	120. ± 8.2
Wind Speed	420. ± 74	360. ± 66	100. ± 17
Relative Humidity	905. ± 375[a]	440. ± 80	145. ± 15
Cum. (Low) Dose	160. ± 15	130. ± 12	43. ± 4.1
Cum. (High) Dose	680. ± 42	430. ± 35	160. ± 9.7

[a] Large range caused by influence of RH on aerosol mass concentration.

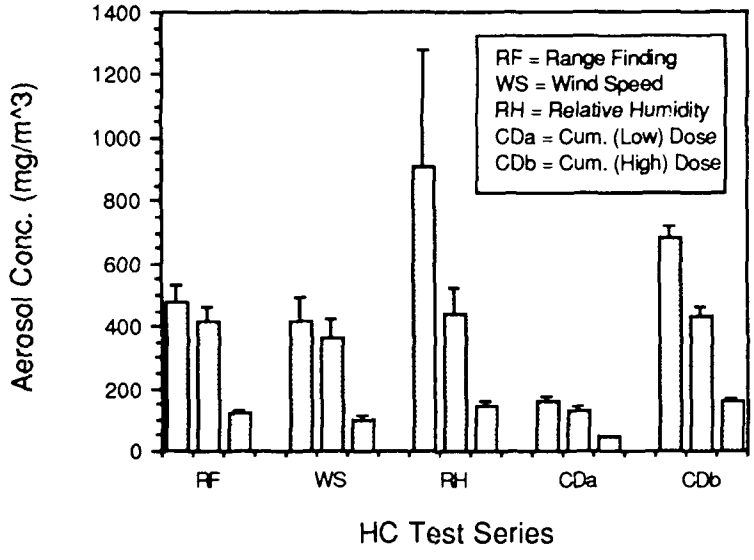


FIGURE 3.1. AVERAGE AEROSOL MASS CONCENTRATIONS IN WIND TUNNEL DURING EACH SERIES OF HC OBSCURANT TESTS

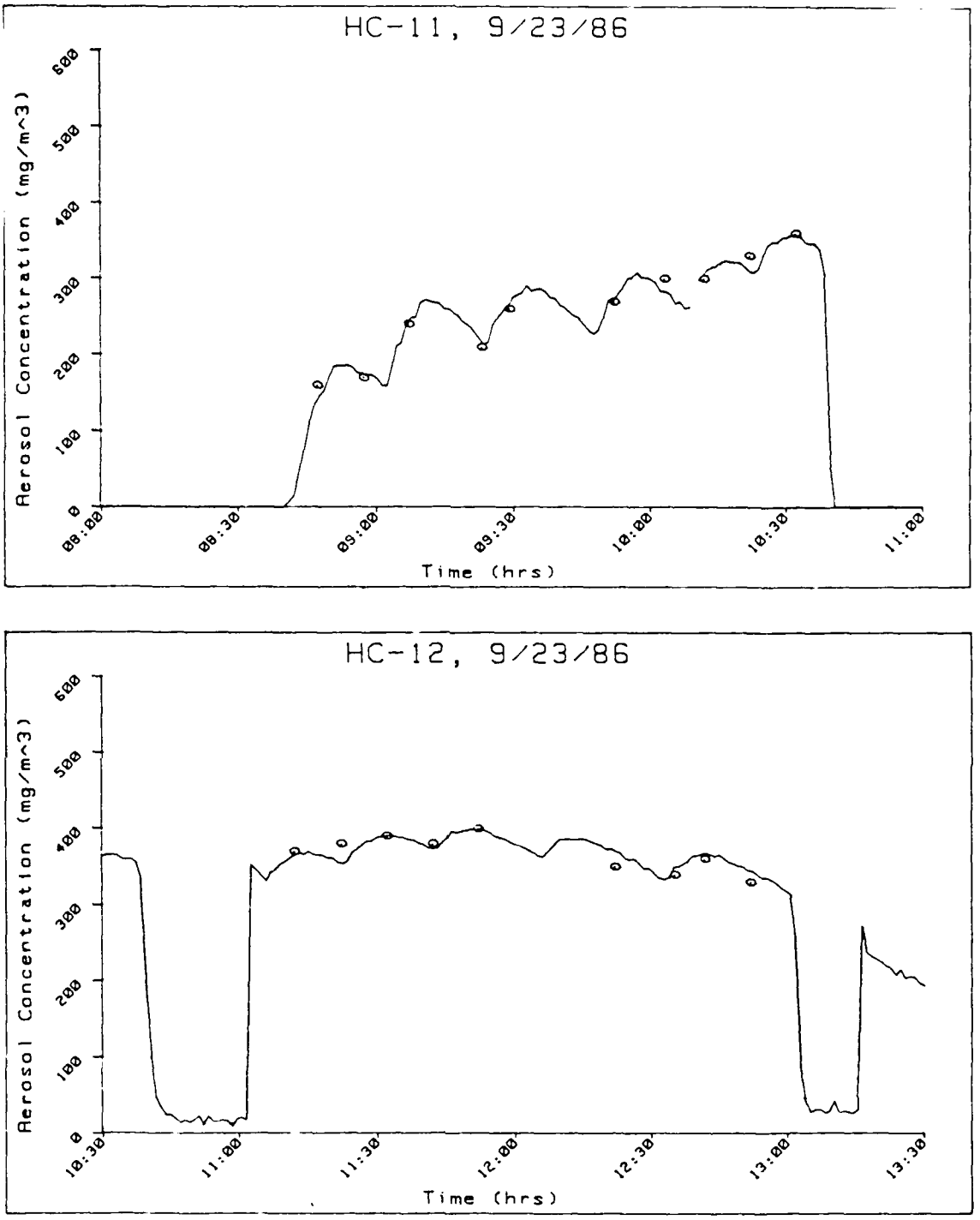


FIGURE 3.2. AEROSOL MASS CONCENTRATION DURING TESTS HC-11 AND HC-12 (WIND SPEED TEST SERIES, 0.9 AND 1.8 m/s, RESPECTIVELY)

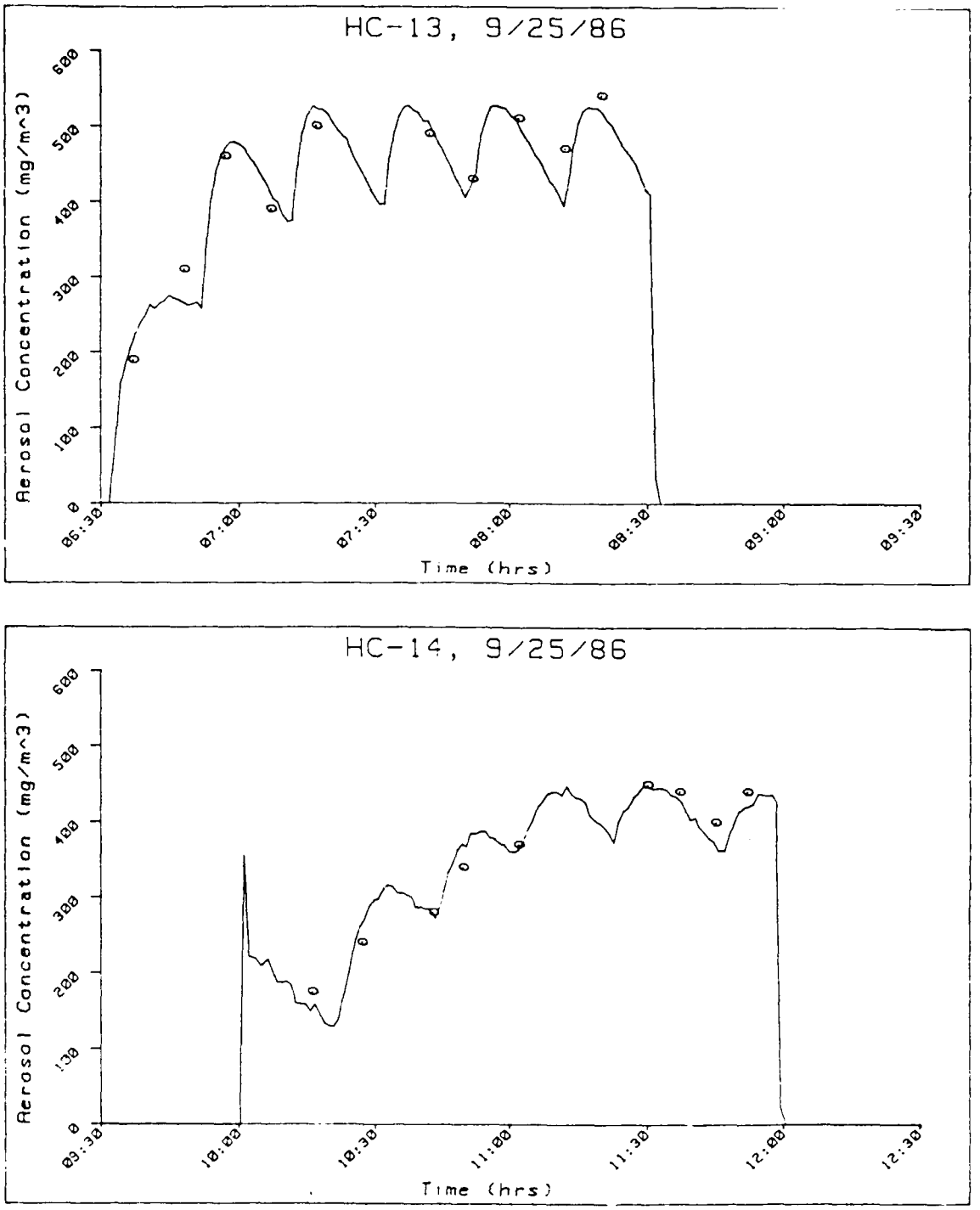
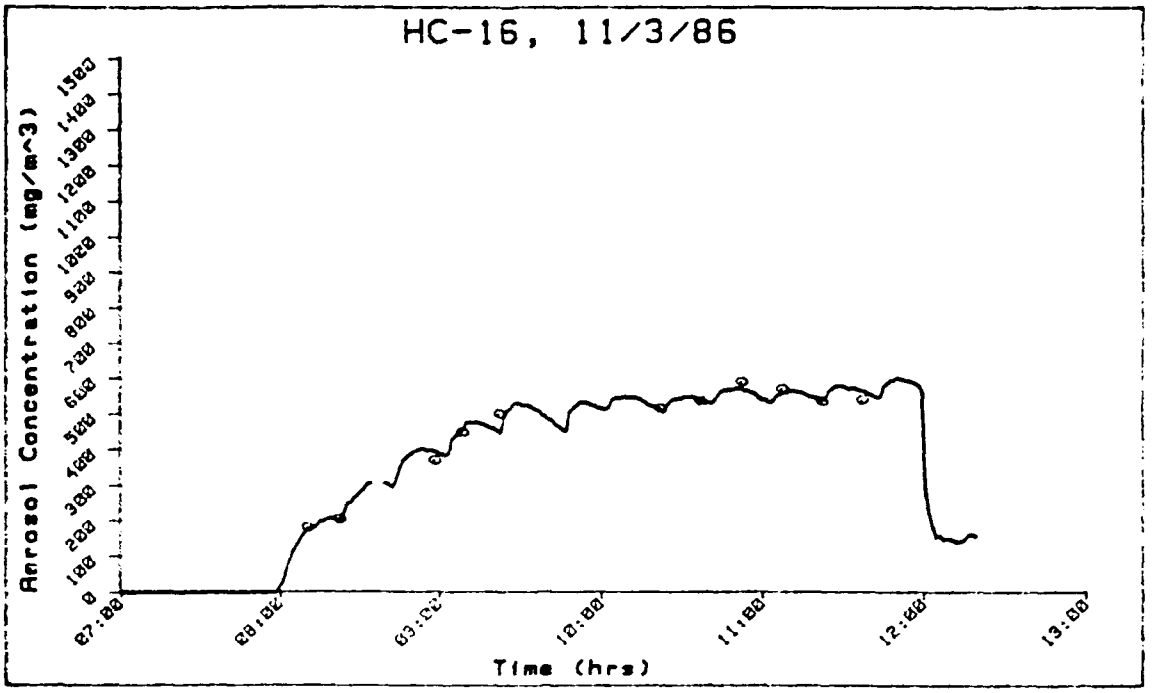


FIGURE 3.3. AEROSOL MASS CONCENTRATION DURING TESTS HC-13 AND HC-14 (WIND SPEED TEST SERIES, 2.8 AND 4.5 m/s, RESPECTIVELY)



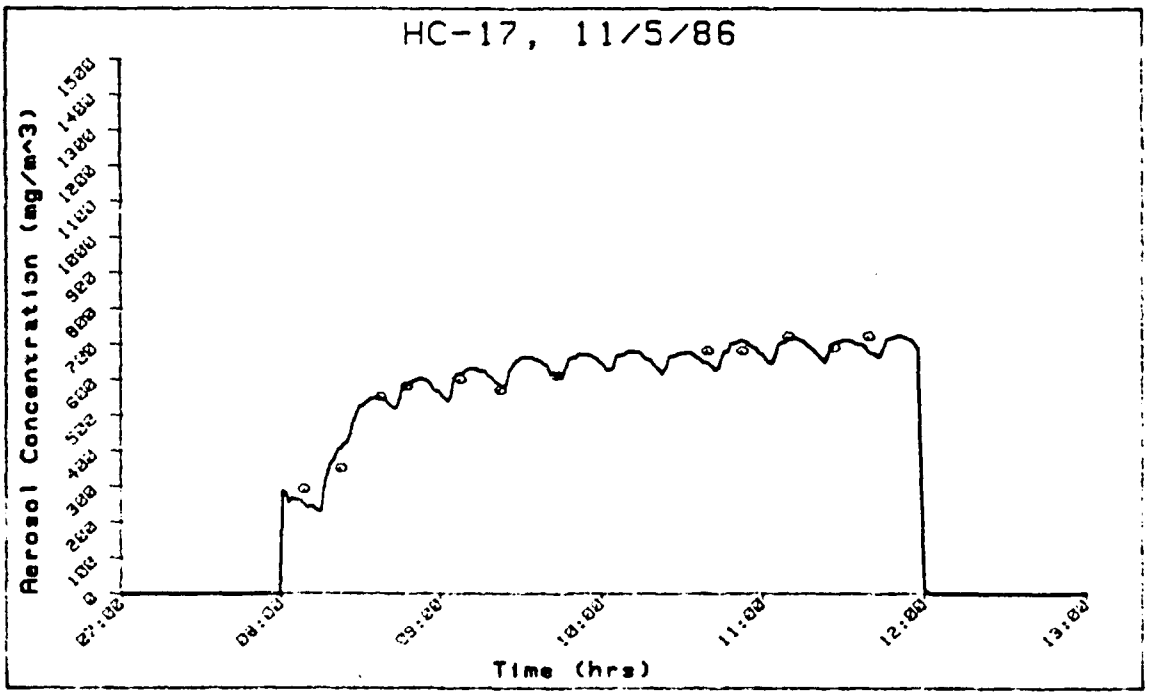
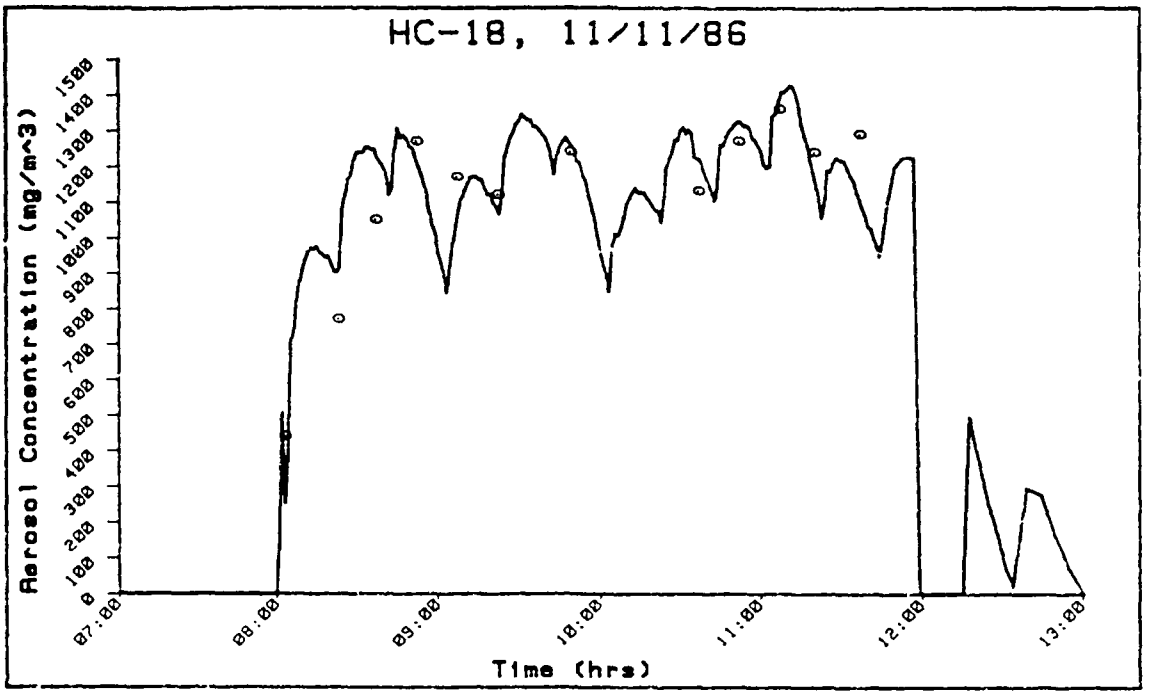


FIGURE 3.4. AEROSOL MASS CONCENTRATION DURING TESTS HC-16 AND HC-17 (RELATIVE HUMIDITY TESTS SERIES, 20 AND 55%, RESPECTIVELY)



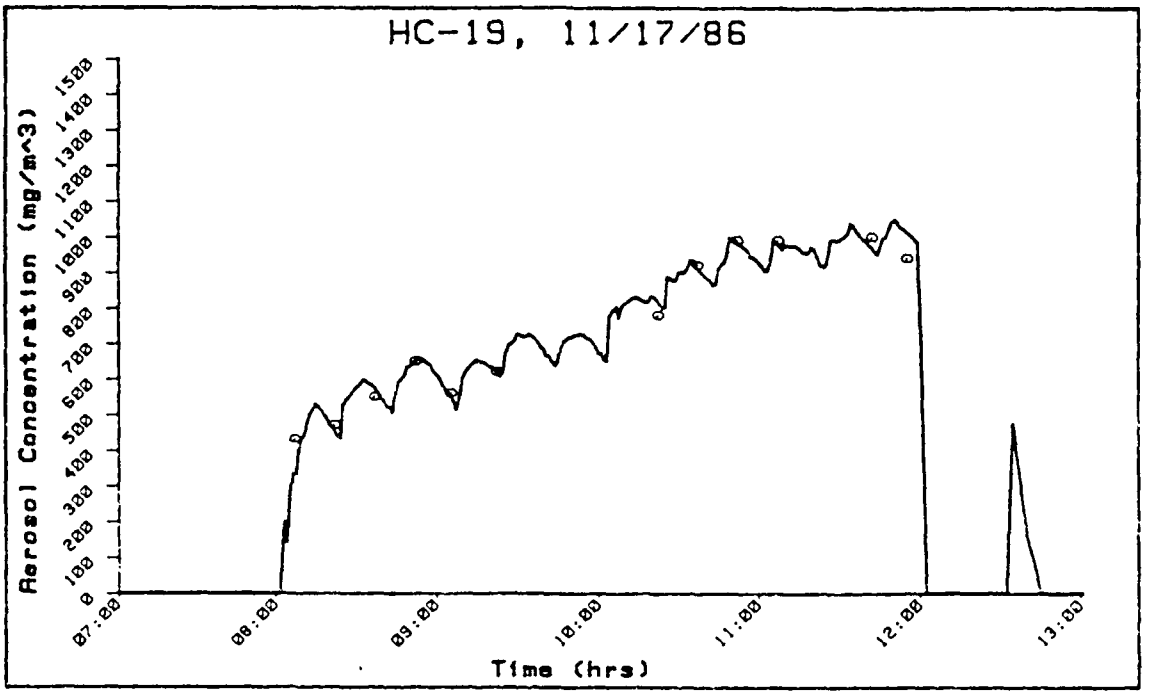


FIGURE 3.5. AEROSOL MASS CONCENTRATION DURING TESTS HC-18 AND HC-19 (RELATIVE HUMIDITY TESTS SERIES, 85% AND SIMULATED-RAINFALL, RESPECTIVELY)

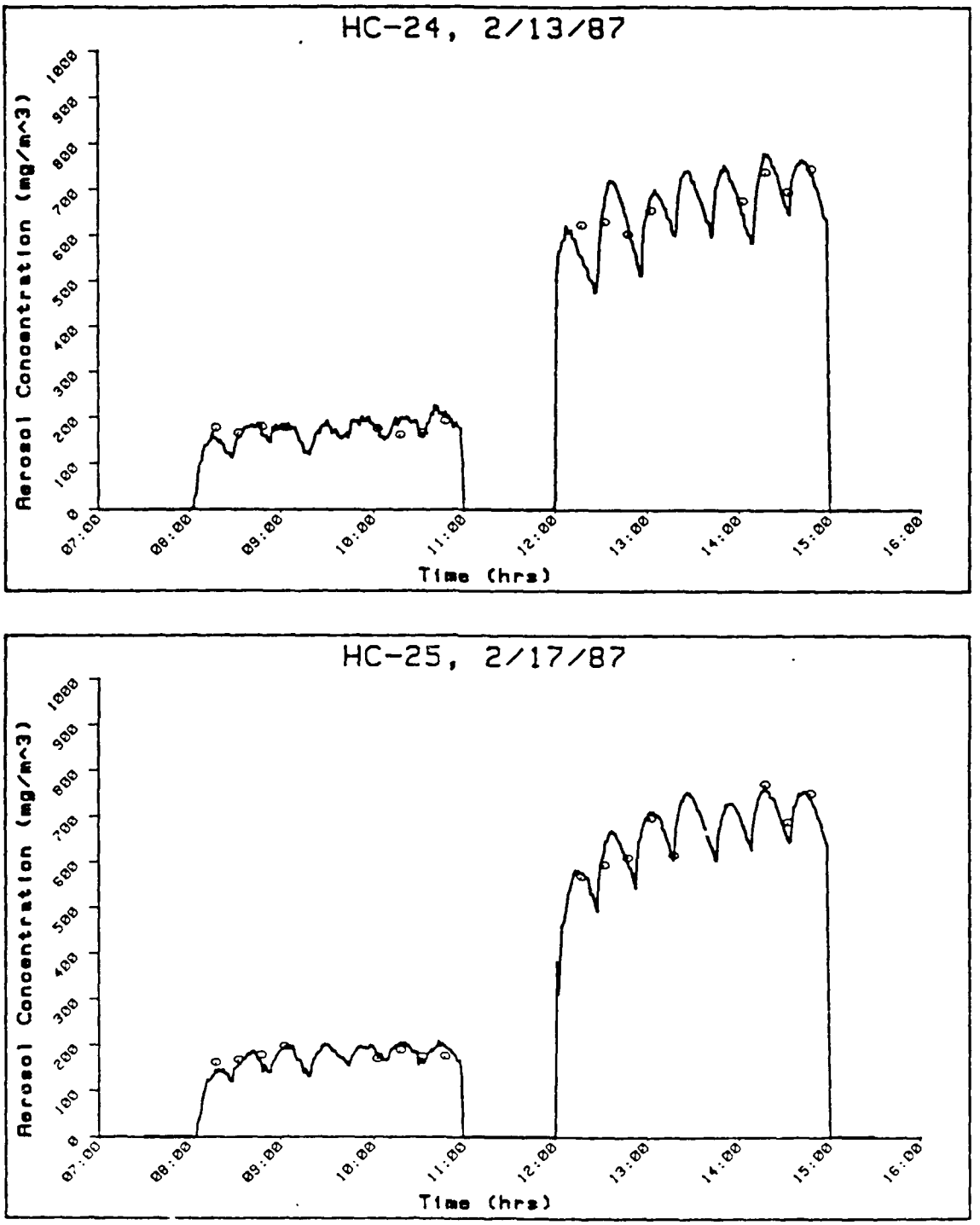


FIGURE 3.6. AEROSOL MASS CONCENTRATION DURING TESTS HC-24 AND HC-25 (CUMULATIVE DOSE TEST SERIES, THIRD AND FOURTH TESTS)

TABLE 3.2. AVERAGE ACTUAL, DESICCATED, AND ZINC AEROSOL MASS CONCENTRATIONS DURING HC OBSCURANT EXPOSURE TESTS IN THE WIND TUNNEL

Test	Relative Humidity (%)	Wind Speed (m/s)	Avg. Aerosol Mass Concentration Actual (mg/m^3)	Desic. (mg/m^3)	Zinc (mg/m^3)
Range-Finding:					
HC-4-3	~40[a]	0.91	430	370	120
HC-5-4	~45[a]	0.90	500	440	120
HC-6-1	~45[a]	0.92	460	400	110
HC-7-2	~45[a]	0.89	540	470	130
Wind Speed:					
HC-9	~50[a]	4.5	450	400	110
HC-11	53	0.89	320	300	83
HC-12	58	1.8	470	435	120
HC-13	69	2.8	490	370	110
HC-14	62	4.5	360	280	83
Relative Humidity:					
HC-16	20	0.88	530	520	130
HC-17	55	0.89	680	500	160
HC-18	85	0.89	1280	360	130
HC-19	66[b]	0.91	850	520	160
Cumulative Dose:					
HC-22a	~40	0.88	129	100[d]	33.5
HC-22b	47	0.88	737	470[d]	181
HC-23a	54	0.88	177	140[d]	47.8
HC-23b	56	0.88	753	480[d]	164
HC-24a	52	0.89	167	130	42.9
HC-24b	52	0.89	654	460	159
HC-25a	52	~0.9	165	120	42.1
HC-25b	53	0.90	656	420	150
HC-26a	53	0.90	156[c]	120[d]	43.2
HC-26b	53	0.89	643	410[d]	159
HC-27a	57	0.90	156	130	42.6
HC-27b	55	0.87	634	410	148
HC-28a	58	~0.9	181[c]	130	48.1
HC-28b	60	0.88	680	370	149
HC-29a	53	0.94	158	120[d]	43.1
HC-29b	52	0.95	681[c]	430[d]	159
HC-30a	54	~0.9	162	140	42.6
HC-30b	53	~0.9	667	420	150

(a) Humidity was measured prior to tests using a constant-draft sling psychrometer.
(b) Simulated rainfall was generated during the second half of HC-19. Humidity increased from 55 to 77%.
(c) Power failure and/or incomplete data record.
(d) Ratio of dried-to-actual particulate matter not determined. Average values for cumulative dosetest series used: 0.79 (low dose), and 0.63 (high dose).

Results of aerosol concentration measurements, listed as average concentrations for each test, are shown in Table 3.2. Listed concentrations were corrected for the influence of sampling probe losses; as shown earlier (Table 2.4) probe correction factors ranged from 1.05 to 1.28, and were typically 1.12. Because of the influence of relative humidity, the actual mass concentration of the HC aerosols varied. However, the desiccated and zinc fractions of the similarly-generated aerosols remained roughly constant. Throughout 13 range-finding, wind speed, and relative humidity tests, the mass concentration of desiccated (nonaqueous) particulate matter was 410 ± 130 mg/m^3, and the average concentration of zinc was 120 ± 40 mg/m^3. A discussion of the relative differences between each of the three primary aerosol concentrations as they were influenced by generation procedures and test environment, is presented in Section 3.1.3.

Because of similar test conditions during the 18 cumulative dose tests, aerosol mass concentrations were approximately uniform: average actual concentration was 160 ± 15 mg/m^3 during the low concentration tests, and 680 ± 40 mg/m^3, or 4.25 times greater, during the high concentration tests. Figure 3.7 shows the average actual HC aerosol mass concentrations during the cumulative dose test series. During the same tests, the average zinc concentrations were 43 ± 10 mg/m^3 during the low concentration tests, and 160 ± 20 mg/m^3, or 3.7 times greater, during the high concentration tests.

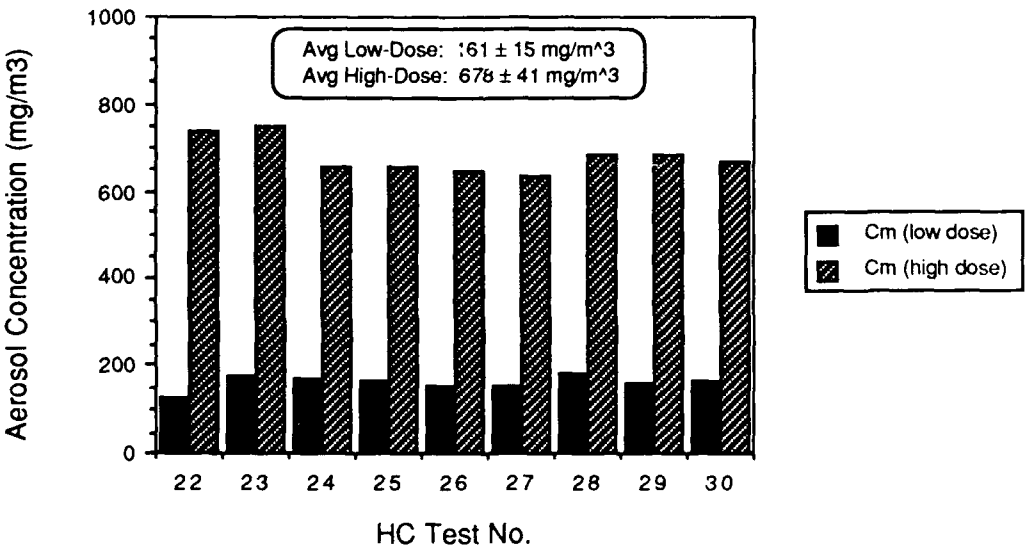


FIGURE 3.7. AVERAGE ACTUAL HC AEROSOL MASS CONCENTRATIONS DURING THE CUMULATIVE DOSE TEST SERIES

When similar aercsol generation procedures were used, measured aerosol mass concentrations were apparently not affected by duration of test or wind speed, but were affected by relative humidity. As relative humidity increased from 20 to 85%, aerosol mass concentration increased about 2.4 times, from 530 to 1280 mg/m^3. This is shown in Figure 3.8. This increase was attributed to an increasing availability of water vapor for condensation and absorption as humidity increased. The increase in aerosol mass concentration was due to a greater fraction of water in the suspended particles: this was verified by the observation that the desiccated aerosol mass concentration did not increase with increasing relative humidity, but remained nearly constant (see Table 3.1, tests HC-16, -17, and -18). That the desiccated aerosol mass concentration was actualy less during the test at 85% humidity was attributed to enhanced sedimentation of the large particles.

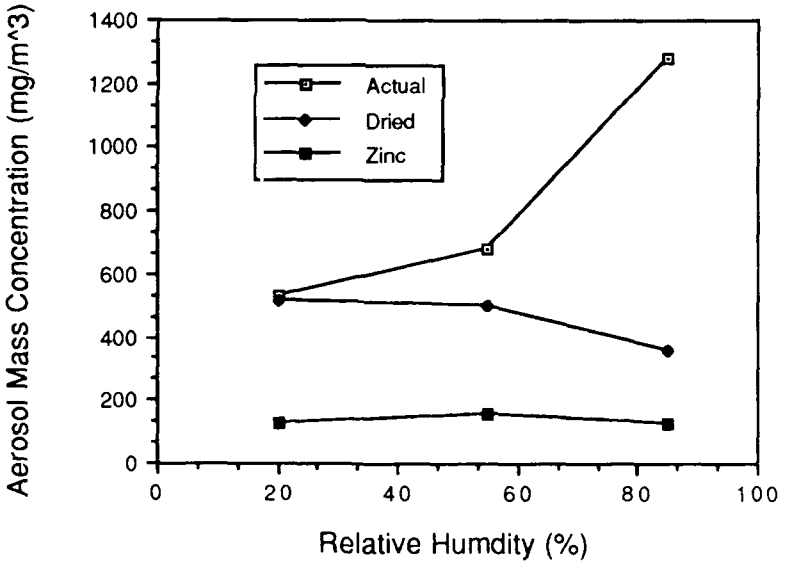


FIGURE 3.8. AVERAGE HC AEROSOL MASS CONCENTRATION VERSUS RELATIVE HUMIDITY DURING TESTS HAVING SIMILAR AEROSOL GENERATION PROCEDURES (HC-16, -17, AND -18)

3.1.2 Particle Size Distribution

The particle size distributions of HC obscurant aerosols were characterized during exposure tests by measuring mass median aerodynamic diameter (MMAD) and geometric standard deviation (GSD) of the suspended particulate material. Because the distribution of particles in the HC aerosols was found to be log-normal, these two parameters combined to provide an adequate description of all HC aerosols generated in the wind tunnel. Results of all particle size distribution measurements are shown in Table 3.3. Particle size distributions from selected tests are shown in Figures 3.9 and 3.10; data shown on the plots represents particulate mass collected on the nine stages of the cascade impactors.

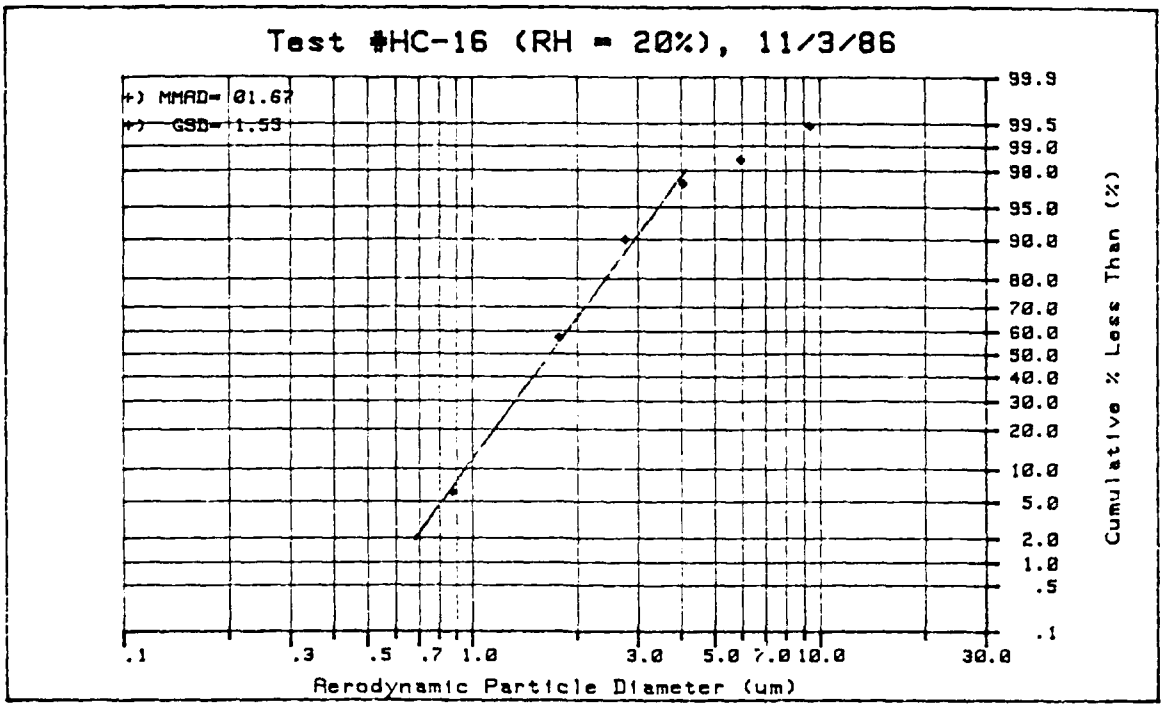
Values for MMAD ranged from 1.3 to 2.1 μm during the HC exposure tests. The data suggest that although wind speed did not appear to have an effect on particle size, both increasing relative humidity and aerosol mass concentration did cause an increase in particle size. As relative humidity increased from 20 to 85%, the MMAD may have increased from 1.7 to 2.1 μm. Assuming an uncertainty of ± 0.1 μm in these measurements, an increase of 1.4 to 2.6 times occurred in the mass concentration of the aerosol as humidity increased. This range roughly corresponds to the mass concentration increase of 2.4 times indicated by the isokinetic filter samples during the same tests. These data also indicate that a threshold, above which most of the effect of relative humidity on particle size distribution occurs (at 22°C), exists at some point between humidities of 60 to 85%. The influence of relative humidity is shown in Figure 3.11; relative particle mass is plotted as $MMAD^3$.

Results of the cumulative dose test series most clearly show the effect of aerosol mass concentration on particle size distribution. Similar results of the relative humidity test series are obscured by the influence of an increasing water content of particles as they grow at the higher humidity. The average MMAD during the low-dose cumulative dose tests was 1.36 ± 0.08 μm, with a GSD of 1.45 ± 0.09, while the MMAD during the high-dose tests was 1.79 ± 0.05 μm, with a GSD of 1.50 ± 0.03. These data indicate that as the aerosol mass concentration increased 3.7 times (from 43 mg/m^3 during the low-dose tests to 160 mg/m^3 during the high-dose tests), the MMAD increased by 1.32 ± 0.12 times. This increase in particle size was attributed to increased particle coagulation during the high-dose tests.

TABLE 3.3. PARTICLE SIZE DISTRIBUTIONS OF HC OBSCURANT AEROSOLS GENERATED WITHIN THE WIND TUNNEL DURING EXPOSURE TESTS

Test	Relative Humidity (%)	Wind Speed (m/s)	Aerosol Conc. (mg/m^3)	Particle Size Distribution MMAD (μm)	GSD (-)
Range-Finding:					
HC-4-3	~40(a)	0.91	430	-	-
HC-5-4	~45(a)	0.90	500	1.9	1.6
HC-6-1	~45(a)	0.92	460	-	-
HC-7-2	~45(a)	0.89	540	-	-
Wind Speed:					
HC-9	~50(a)	4.5	450	2.0	1.5
HC-11	53	0.89	320	1.6	1.5
HC-12	58	1.8	470	1.7	1.5
HC-13	69	2.8	490	1.5	1.4
HC-14	62	4.5	360	1.6	1.4
Relative Humidity:					
HC-16	20	0.88	530	1.7	1.6
HC-17	55	0.89	680	1.8	1.5
HC-18	85	0.89	1280	2.1	1.5
HC-19	66(b)	0.91	850	-	-
Cumulative Dose:					
HC-22a	~40	0.88	129	-	-
HC-22b	47	0.88	737	1.75	1.5
HC-23a	54	0.88	177	1.44	1.5
HC-23b	56	0.88	753	1.84	1.5
HC-24a	52	0.89	167	1.32	1.4
HC-24b	52	0.89	654	1.78	1.5
HC-25a	52	~0.9	165	-	-
HC-25b	53	0.90	656	-	-
HC-26a	53	0.90	156	-	-
HC-26b	53	0.89	643	-	-
HC-27a	57	0.90	136	-	-
HC-27b	55	0.87	634	1.81	1.5
HC-28a	58	~0.9	181	-	-
HC-28b	60	0.88	680	-	-
HC-29a	53	0.94	158	1.31	1.4
HC-29b	52	0.95	681	1.77	1.5
HC-30a	54	~0.9	162	-	-
HC-30b	53	~0.9	667	-	-

(a) Humidity was measured prior to tests using a constant-draft sling psychrometer.
(b) Simulated rainfall was generated during the second half of HC-19. Humidity increased from 55 to 77%.



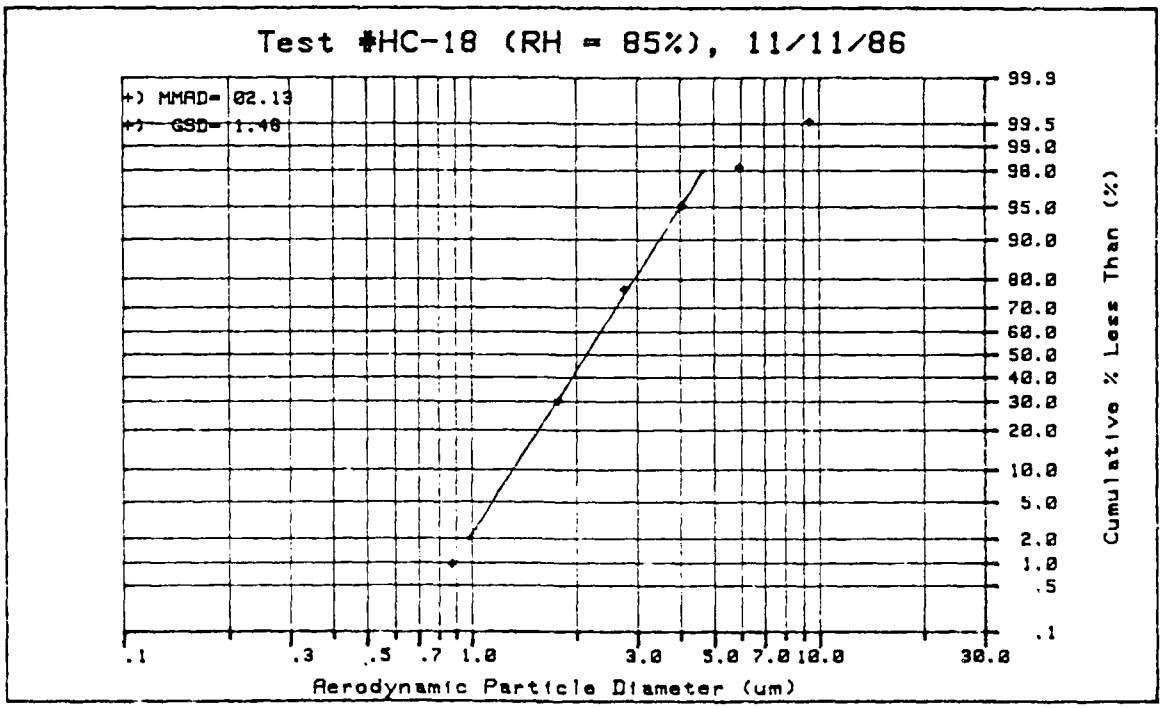
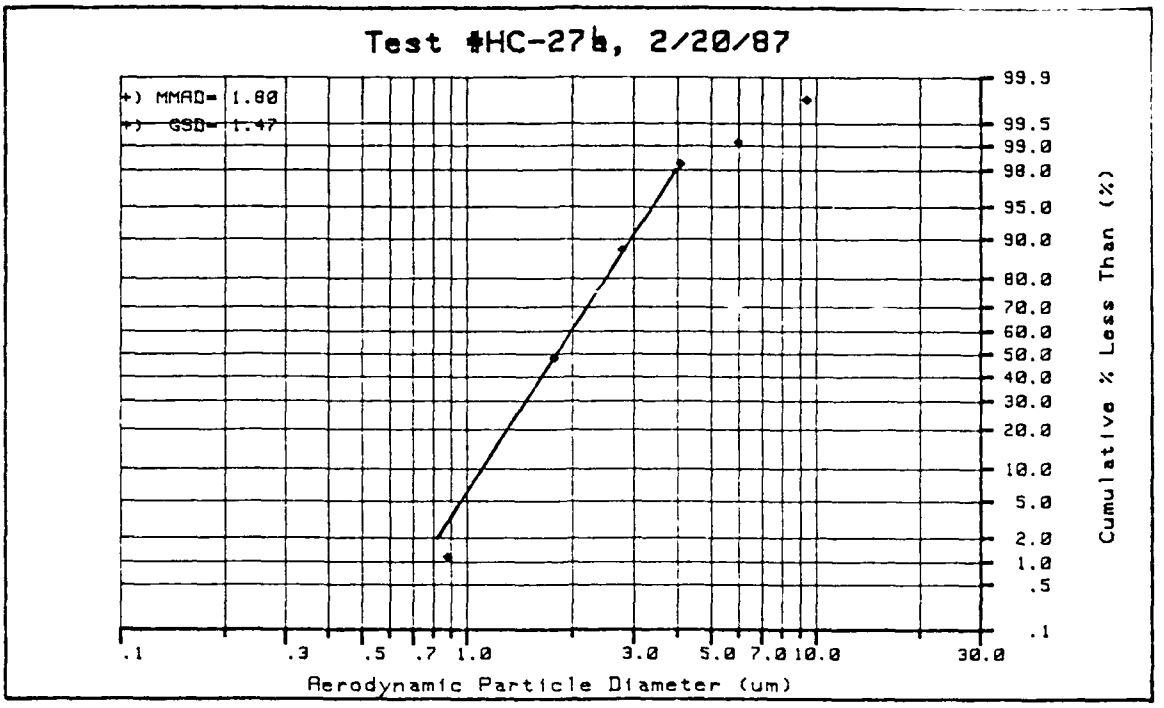


FIGURE 3.9. AERODYNAMIC PARTICLE SIZE DISTRIBUTION OF HC AEROSOLS DURING TESTS HC-16 (20% RH) AND HC-18 (85% RH)



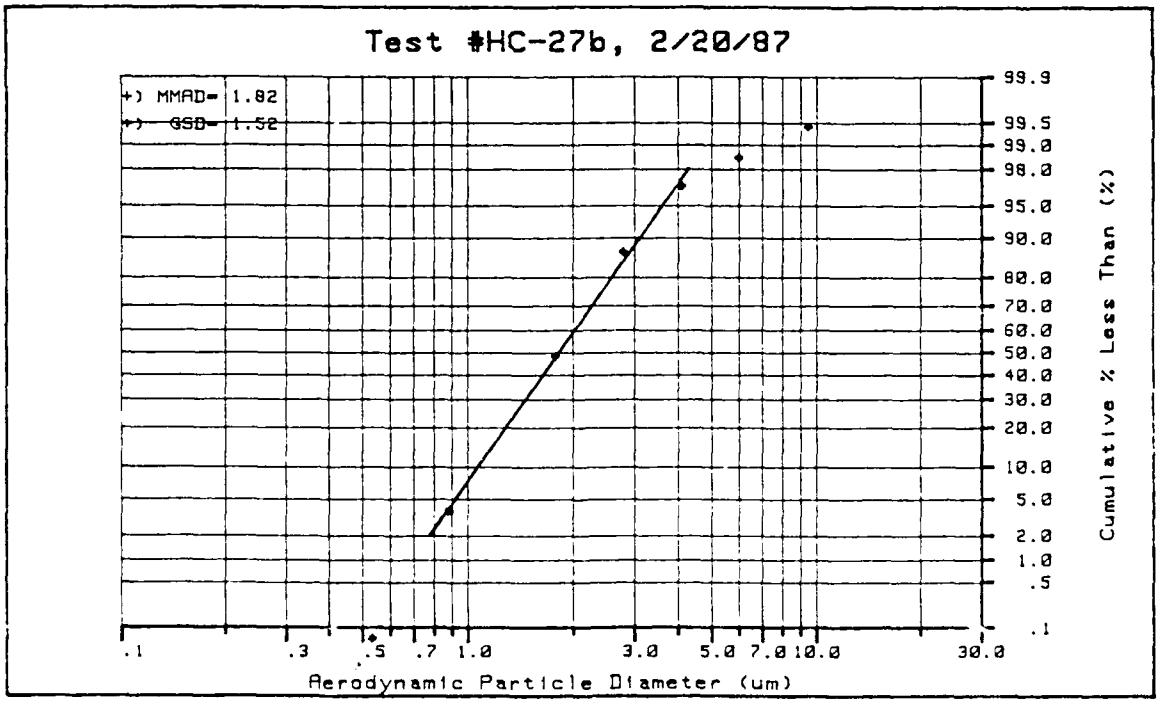


FIGURE 3.10. AERODYNAMIC PARTICLE SIZE DISTRIBUTION OF HC AEROSOLS DURING CUMULATIVE DOSE TEST HC-27a (LOW-DOSE) AND HC-27b (HIGH-DOSE)

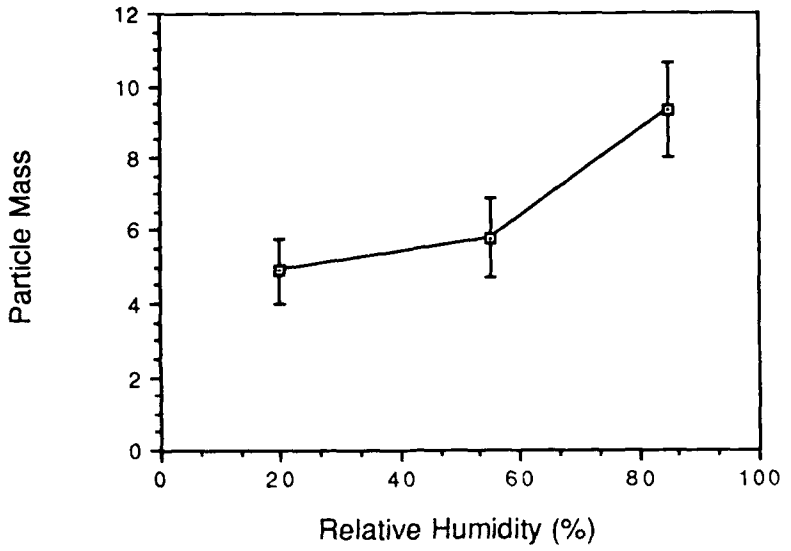


FIGURE 3.11. INFLUENCE OF RELATIVE HUMIDITY ON PARTICLE MASS ($MMAD^3$)

3.1.3 Aerosol Chemical Composition

Results of measurements of the bulk composition of HC aerosols are discussed in this section. Both the percentage of the aerosols as water and the percentage as zinc are discussed. Additional measurements of the inorganic and organic constituents of the aerosols are discussed in Sections 3.2.1 and 3.2.2.

The ratios of dried particulate mass and zinc mass to fresh, or actual, aerosol mass was seen to be influenced by the relative humidity. Data were obtained during most tests and are summarized in Table 3.4 and shown in Figure 3.12. The HC aerosols were seen to be about 22 to 28% (average = 23%) zinc, by mass, for humidities between 20 and 65%. At higher humidities the zinc percentage rapidly decreased to less than 10% at a relative humidity of 85%. This was attributed to the water absorbed by the particles that increased their mass by two or three times. This water gain at high humidities was also observed by comparing desiccated to actual particulate mass--the difference being attributed primarily to the fraction of the suspended particles consisting of water. The nonevaporating fraction of the HC aerosols was seen to decrease from greater than 95% to about 30% as humidity increased from 20 to 85%. For midrange humidities (20 to 65%), the nonevaporating fraction of the aerosols was not clearly defined, but generally ranged between 65 and 90%.

TABLE 3.4. BULK HC AEROSOL COMPOSITION MEASUREMENTS FOR PERCENTAGE DRIED PARTICULATE MATTER AND PERCENTAGE ZINC

Test	Relative Humidity (%)	% of Actual Sample Mass (n = No. of Samples) Desiccated (Fraction)	(n)	Zinc (Fraction)	(n)
Range-Finding:					
HC-4-3	~40[a]	-	-	0.283 ± 0.011[b]	4
HC-5-4	~45[a]	0.871 ± 0.012	5	0.248 ± 0.017	4
HC-6-1	~45[a]	-	-	0.243 ± 0.004	2
HC-7-2	~45[a]	-	-	0.252 ± 0.009	3
Wind Speed:					
HC-9	~50[a]	-	-	0.234 ± 0.023	4
HC-11	53	0.927 ± 0.035[b]	6	0.256 ± 0.036	4
HC-12	58	0.917 ± 0.035	5	0.256 ± 0.015	4
HC-13	69	0.754 ± 0.057	5	0.214 ± 0.007	4
HC-14	62	0.800 ± 0.043	6	0.232 ± 0.005	4
Relative Humidity:					
HC-16	20	0.970 ± 0.047	4	0.260 ± 0.006	4
HC-17	55	0.742 ± 0.073	4	0.224 ± 0.014	4
HC-18	85	0.283 ± 0.034	7	0.103 ± 0.005	4
HC-19[c]	55	0.759 ± 0.065	5	0.225 ± 0.002	2
HC-19[c]	77	0.449 ± 0.068	5	0.134 ± 0.006	2
Cumulative Dose:					
HC-22a-30a	52.6 ± 5.2	0.790 ± 0.075	14	0.268 ± 0.013	33
HC-22b-30b	53.4 ± 3.5	0.626 ± 0.054	14	0.232 ± 0.014	36

(a) Humidity was measured prior to tests using a constant-draft sling psychrometer.
(b) Uncertainty = one standard deviation for n > 2. For n = 2, uncertainity = range of data.
(c) Simulated rainfall was generated during the second half of HC-19. Humidity increased from 55 to 77%.

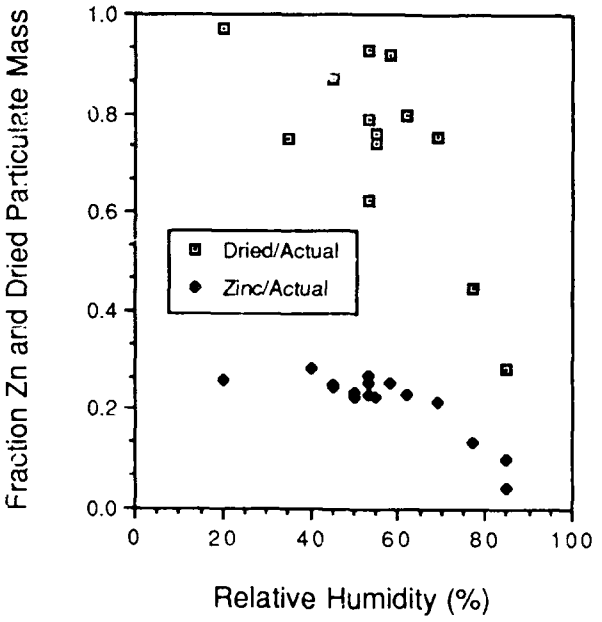


FIGURE 3.12. PERCENTAGE ZINC AND DESICCATED PARTICULATE MASS PER ACTUAL MASS OF HC AEROSOLS COLLECTED ON GLASS FIBER FILTERS

The ratio of zinc mass to dried particulate mass was roughly constant during the tests. The percentage zinc was 29.3 ± 2.7% for the 12 tests analyzed during the early tests; however, the ratio increased to 33.9% during the low-dose cumulative dose tests, and 37.1% during the high-dose tests. The reason for this variation in zinc percentage of the dried particulate mass was not apparent; however, possible reasons for shifting zinc percentage include test humidity, laboratory humidity, temperature, aerosol mass concentration, and aging time.

3.1.4 Deposition Velocity to Suspended Surrogate Surfaces

The rate of deposition, or deposition velocity, of HC aerosols to surrogate surfaces was determined to provide comparison with deposition velocities measured to plant and soil surfaces. The surrogate surfaces employed were 47-mm glass fiber filter deposition coupons that were suspended, on stiff springs, horizontally in the wind tunnel test section just upwind of the test subjects. Results of HC aerosol deposition to plant and soil surfaces, and other surrogate surfaces such as dry and wet petri dishes are presented elsewhere.

Desiccated and zinc particulate masses deposited to each filter coupon during the tests were compared to the product of the surface area of the coupon, the average concentration of aerosol during the test, and the time of exposure to determine the deposition velocity. The resulting deposition velocity was determined in units of centimeters per second (cm/s). Surface area was calculated as two times the surface area of the filter coupons minus 0.7 cm^2, which was the area covered by the suspending spring. Calculated deposition velocities were then compared to test conditions, primarily wind speed, but also aerosol mass concentration. An increase in deposition velocity with increasing particle size may also be expected; however, these results were incorporated in the influences of increasing concentration and humidity as discussed in previous sections.

The deposition velocity of HC aerosols was seen to increase with increasing wind speed and aerosol mass concentration. An indication of an increase with increasing relative humidity was also noted and reflected increasing aerosol mass concentration and the resulting particle size increase caused by absorption of water vapor. These results are shown in Figures 3.13 and 3.14. Deposition velocities are shown for both dried and zinc particulate mass. No obvious difference in the rate of deposition was observed between the dried and zinc particulate masses under varying wind speeds, but the rate of deposition of zinc did appear to be about 20% less than that of dried particulate mass for constant wind speed and varying aerosol mass concentration and relative humidity.

The increase of deposition velocity was most significant as wind speed increased. Deposition velocities for dried particulate mass ranged from about 0.0094 ± 0.0040 cm/s at 0.9 m/s to 0.063 ± 0.025 cm/s at 4.5 m/s. Under similar conditions, the deposition velocity of zinc mass increased from 0.0083 ± 0.0044 to 0.054 ± 0.023 cm/s. Although the deposition velocity increased with increasing wind speed, the figures show that this increase was not linear. The rate of increase in deposition velocity was most noticeable between 2.8 and 4.5 m/s. Between 0.9 and 2.8 m/s, deposition velocity only increased by 1.5 to 2.3 times, but between 2.8 and 4.5 m/s, the increase was 2.9 to 4.5 times. Deposition velocities are anticipated to increase at even greater rates at wind speeds greater than those tested. The large uncertainty values for deposition velocities measured at 4.5 m/s were due in part to the limited number of samples considered, but were primarily caused by the different response of the six suspended coupons to large wind forces and turbulence--some of the filters tended to vibrate more than others as they were buffeted by wind forces. An earlier trial test at 4.5 m/s did not produce usable data as most of the coupons were insufficiently mounted and were blown against the support spring and did not remain horizontal throughout the test.

The deposition velocities measured at the lower wind speeds were compared to still-air settling of similarly sized particles. The mass median aerodynamic diameter of the

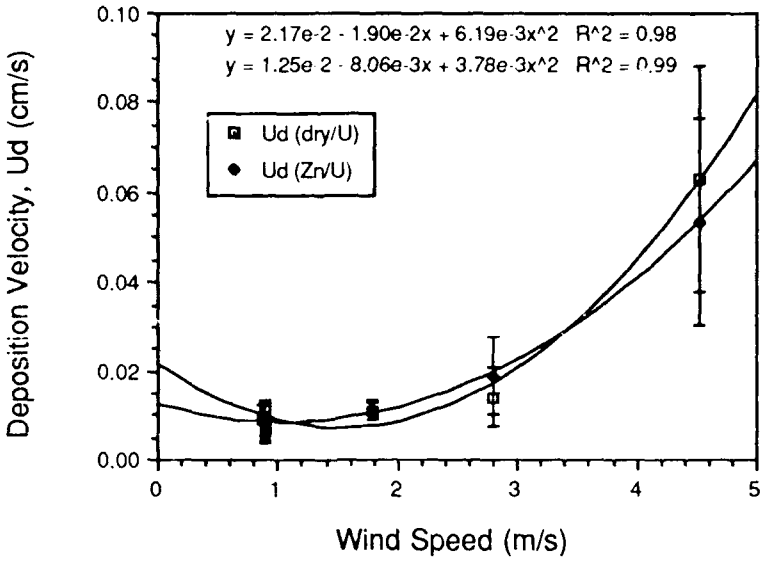


FIGURE 3.13. THE INFLUENCE OF WIND SPEED ON DEPOSITION VELOCITY OF HC AEROSOL TO GLASS FIBER FILTER SURFACES SUSPENDED HORIZONTALLY IN THE WIND TUNNEL TEST SECTION

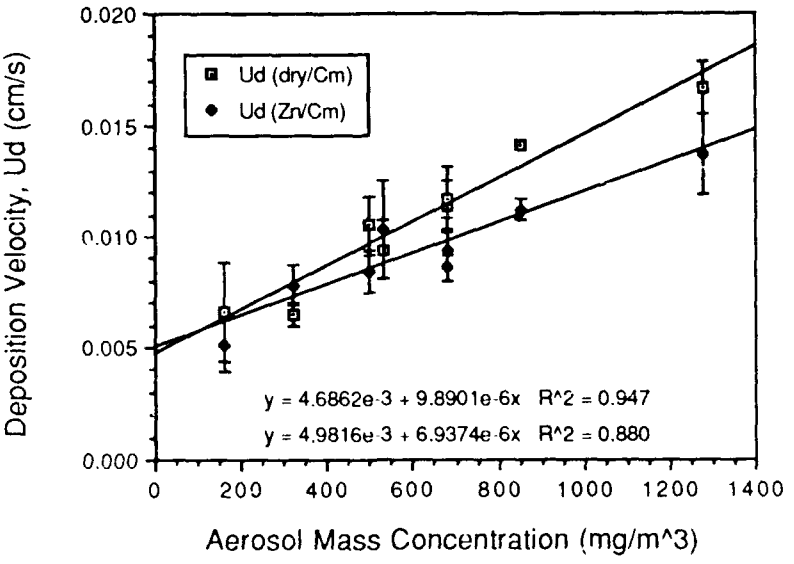


FIGURE 3.14. THE INFLUENCE OF AEROSOL MASS CONCENTRATION ON DEPOSITION VELOCITY OF HC AEROSOL TO GLASS FIBER FILTER SURFACES SUSPENDED HORIZONTALLY IN THE WIND TUNNEL TEST SECTION

particles was about 2 μm with 80% of the particulate mass consisting of particles between 1 and 3 μm. These particle sizes correspond to still-air settling rates of 0.004 and 0.03 cm/s (Hinds 1982), a range that included the measured deposition velocities of about 0.009 cm/s.

Aerosol mass concentration influenced the deposition rate of HC aerosols only to a small degree. It is speculated that the measured increases in deposition velocity were caused by sedimentation of larger particle sizes created by coagulation as aerosol mass concentration increased, and by absorption of water vapor at high humidities. Deposition velocity of dried particluate mass increased about 2.5 times, from 0.0066 ± 0.0022 to 0.0167 ± 0.0012 cm/s as aerosol mass concentration increased from 160 to 1280 mg/m^3. Measured deposition velocities of zinc mass were about 20% less than those for dried particulate mass and increased from 0.0051 ± 0.0012 to 0.0137 ± 0.0018 cm/s. The reason for this was not apparent as preferential coagulation or water vapor attraction of particles with potentially lesser percentages of zinc would not be anticipated due to the hygroscopic nature of $ZnCl_2$. The increase in deposition velocity with increasing aerosol mass concentration was uniform over the range of concentrations studied, unlike the nonlinear effect of increasing wind speed.

3.2 CHEMICAL CHARACTERISTICS OF HC SMOKES

The basic equations suggested as basis of the formation of HC smoke are as follows:

$$2\,Al + C_2Cl_6 + 3\,ZnO = 3\,ZnCl_2 + Al_2O_3 + 2\,C + Heat \qquad (1)$$

$$2\,Al + 3\,C_2Cl_6 + 9\,ZnO = 9\,ZnCl_2 + Al_2O_3 + 6\,CO \qquad (2)$$

Equation (1) stoichiometry approximates the upper layer of the smoke pot, with higher A1 content, while Equation (2) stoichiometry approximates the bulk of the smoke pot. A combination of the reactions is probably involved in actual deployments. Earlier limited studies (Katz et al. 1980) comparing laboratory simulations with field deployment of an actual M5 canister found considerable discrepancies in detected reaction products, particularly in the amount of HCl found.

3.2.1. Organic Characterization of Aerosols

Prior to analysis of organic residues produced by combustion of hexachloroethane mixtures, estimated chlorocarbon concentrations were based on observed values of other investigators, however, expected or theoretical chlorocarbon concentrations determined by Cichowicz (1983) and Katz et al. (1980) ranged from 1 to 15 times less than the maximums reported. The difference likely results from the fact that a large portion of the C_2Cl_6 and

C_6Cl_6 aerosolized is in condensed (particulate) form and would not therefore be sampled by the chromatograph but rather would be deposited to the walls of the sampling tubes during transport. These compounds would be more likely to be retained on the glass fiber air and deposition samples than would the more volatile CCl_4 and C_2Cl_4. Perhaps the most accurate measurement of total chlorocarbons is that associated with the liquid impinger samples, where both the gaseous and particulate fractions of the HC aerosols are trapped.

The concentration of chlorocarbons in the wind tunnel gaseous phase was monitored as the HC smoke generation progressed during experiments. Several problems with the initial design of the automatic on-line sampling gas chromatograph, which were discovered during the wind speed test, prevented the instrument from obtaining complete data sets. These problems were associated with the original timing method used for switching the sample stream selection valve and the sampling loop valve. The problems were corrected and the sampling system was on line for the relative humidity (RH) tests HC-16 (20% RH), HC-17 (55% RH), HC-18 (90% RH), and HC-19 (first half 55% RH, second half 95% RH). The four compounds monitored were carbon tetrachloride (CCl_4), tetrachloroethene (C_2Cl_4), hexachloroethane (C_2Cl_6), and hexachlorobenzene (C_6Cl_6). Table 3.5 gives the average concentration measured for each compound over the time that the test took place. These were the only compounds detected using the sampling method described. Had any other similar chlorocarbons been present they would have also been detected.

In all four of the humidity tests C_2Cl_4 was present at the highest concentration, with an average concentration of 3 mg/m^3, four to five times greater than the other chlorocarbons. The gaseous concentrations of the three other chlorocarbons ranged from 0.7 to 0.9 mg/m^3. No significant trends for either the individual or total chlorcarbons were noted with changes in relative humidity.

TABLE 3.5. AVERAGE CHLOROCARBON CONCENTRATION MEASURED IN WIND TUNNEL TEST SECTION DURING RELATIVE HUMIDITY TESTS

	CCl_4 (mg/m^3)	C_2Cl_4 (mg/m^3)	C_2Cl_6 (mg/m^3)	C_6Cl_6 (mg/m^3)	Total (mg/m^3)
HC16	1.3	4.4	0.64	0.81	7.1
HC17	0.65	2.6	1.26	0.63	5.2
HC18	0.69	2.9	0.99	0.42	5.0
HC19	0.68	2.2	0.67	[illegible]	4.5
Average	0.82	3.0	0.89	0.69	
Std. Dev.	0.30	0.94	0.30	0.21	

Figure 3.15 shows the measured gaseous air concentrations of the four chlorocarbons over the exposure period for each test series. During HC-16, and to some extent tests HC-17 through HC-19, the C_6C_{l6} concentration seemed to have several unexplainable peaks. These peaks in concentration did not appear to be caused by spurious detector responses because peaks were not observed for the other three compounds. It was initially assumed that these spurious concentration increases may have resulted from the periodic burning of new HC pots as the test progressed. However, the periodicity of the C6Cl6 peak concentration increased with time and was greater than 30 min, whereas the smoke pots were ignited at set time intervals of 15 to 25 min, and the durations of the peaks were much greater than the duration of HC-pot combustion (~13 s). Because this phenomena was observed principally in the HC-16 test and was not observed in later (cumulative dose) tests, it was dismissed as an unusual occurrence.

After the relative humidity tests were completed, the on-line GC's gas sampling valves were dismantled and cleaned. A significant amount of particulate deposits were found in the sampling valves. Thus, the spurious concentration peaks may have arisen from revolatilization of organic residues during the sample line heating cycle. To alleviate this problem, a high-efficiency particulate filter was added to the sampling lines between the wind tunnel test section and the stream selection valve. A Valco® stream selection module and a multiposition control module were added to the system to give greater control and flexibility over the valve movement. The system was recalibrated and put back into operation for the cumulative dose tests.

The air concentrations of CCl_4, C_2Cl_4, and C_2Cl_6 measured in the wind tunnel test section during the series of cumulative dose experiments are given in Figures 3.16 and 3.17. In Figure 3.16 the the concentrations the individual compounds measured in HC-23 through HC-30 are plotted together. This allows a direct intracomparison of the concentrations between tests. The concentration of the chlorocarbons measured in the individual tests are plotted in Figure 3.17 to allow intracomparison of the individual compound concentrations.

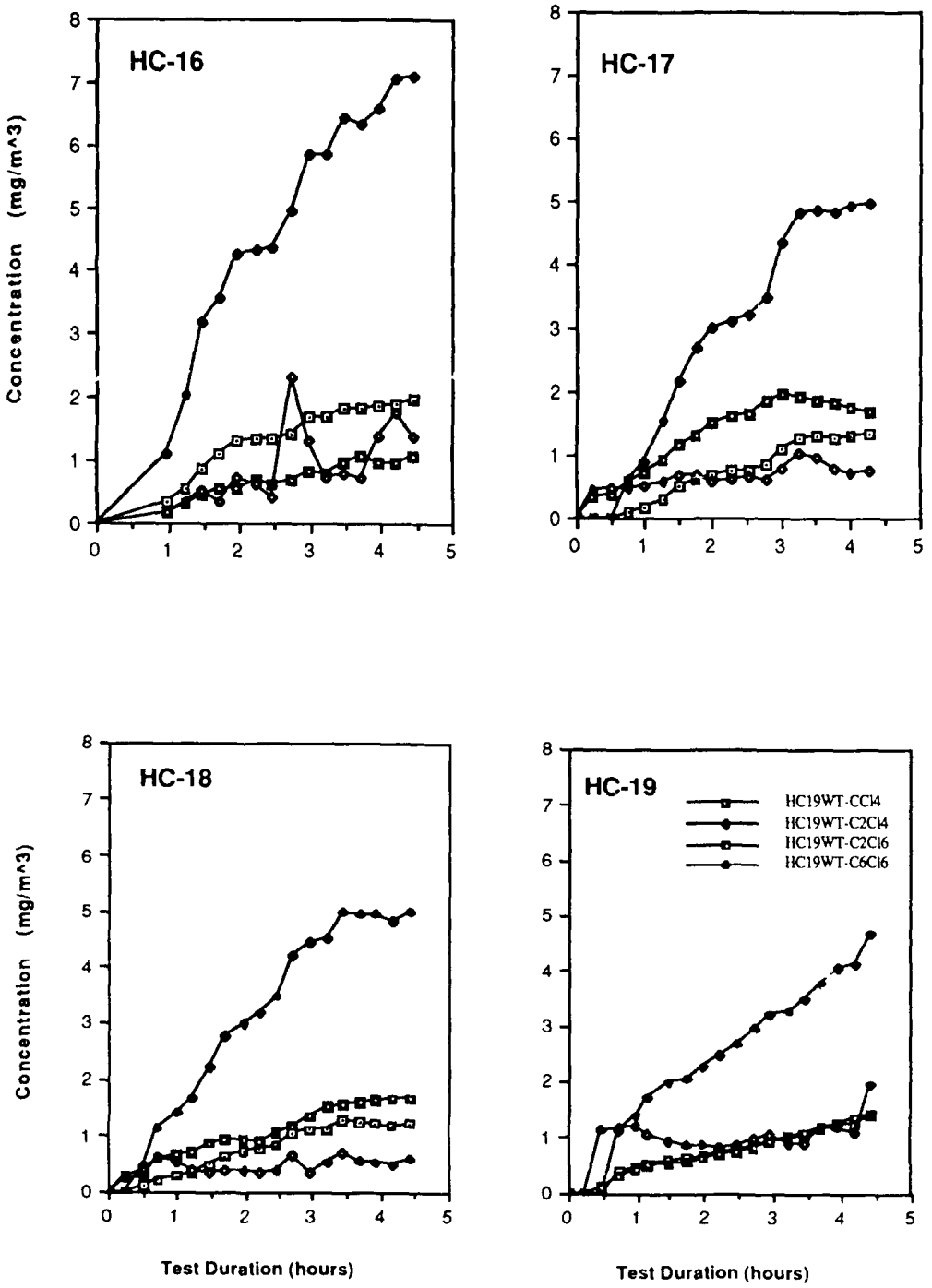


FIGURE 3.15. CONCENTRATIONS OF CCl_4, C_2Cl_4, C_2Cl_6, AND C_6Cl_6 IN WIND TUNNEL TEST SECTION DURING THE RELATIVE HUMIDITY TESTS

Apparently C_6Cl_6, which may be primarily in particulate form, was removed by the filter placed between the test section and the stream selection valve, as it was not found at quantifiable concentrations during any of the cumulative dose tests. This is not too surprising as the vapor pressure of hexachlorobenzene is low enough that it should be primarily associated with the particulate aerosol, and therefore collected by the filter.

It should be noted that the measured concentrations were plotted against the relative time the samples were taken. Because the gas chromatograph was manually started before the test actually began, there is much as a 20-min difference between the beginning of the gas sampling and when the actual experiment was initiated. Thus a slight time shift can be seen between some of the overlaid plots.

There are several discontinuities in the data sets collected during some of the cummulative dose experiments, evident by the data gaps shown in the plots. An intermittent problem occurred during several tests, affecting the compressed air line the feeding the stream selection valve. The pressure decrease caused the sampling valve to malfunction periodically. Although some data were lost, the goal of the air monitoring during these generation periods was primarily to ensure that the burns were progressing in a similar manner from day to day. In spite of the missing data, it is clear from the graphs in Figure 3.15 that this was the case.

The plots in Figure 3.16 clearly show a sharp discontinuity in the concentration of the compounds between 3 and 4 h after the test began. This can also be seen in Figure 3.17. This discontinuity is the point the larger pots were set off to give a higher concentration of the aerosol. The sharp spike in concentrations evident in several of the experiments during this transition period may have been caused by the sampling valve opening just as HC smoke generated from burning one of the larger HC pots was released from the combustion chamber, cycled one time through the wind tunnel, and passed the GC sampling port. By the next sampling period, the peak concentrations had been diluted to a level that was consistent with the steadily increasing concentration of the compounds in the test section.

It appears that in the cumulative dose experiments, CCl_4 was produced at a increased rate during the second half of the tests when the larger HC pots were being ignited. This is evident in the plots given in Figure 3.17. At the point of increase, the concentration of CCl_4 became greater than C_2Cl_6, and remained that way until the end of the experiment. The chemical composition of the large and small pots are the same, and they are identical in all respects except for the total mass of material. However, the larger pots do burn at an increased rate, and this may result in an increased combustion temperature. In most cases the C_2Cl_4 appears to build in concentration at about the same rate, regardless of

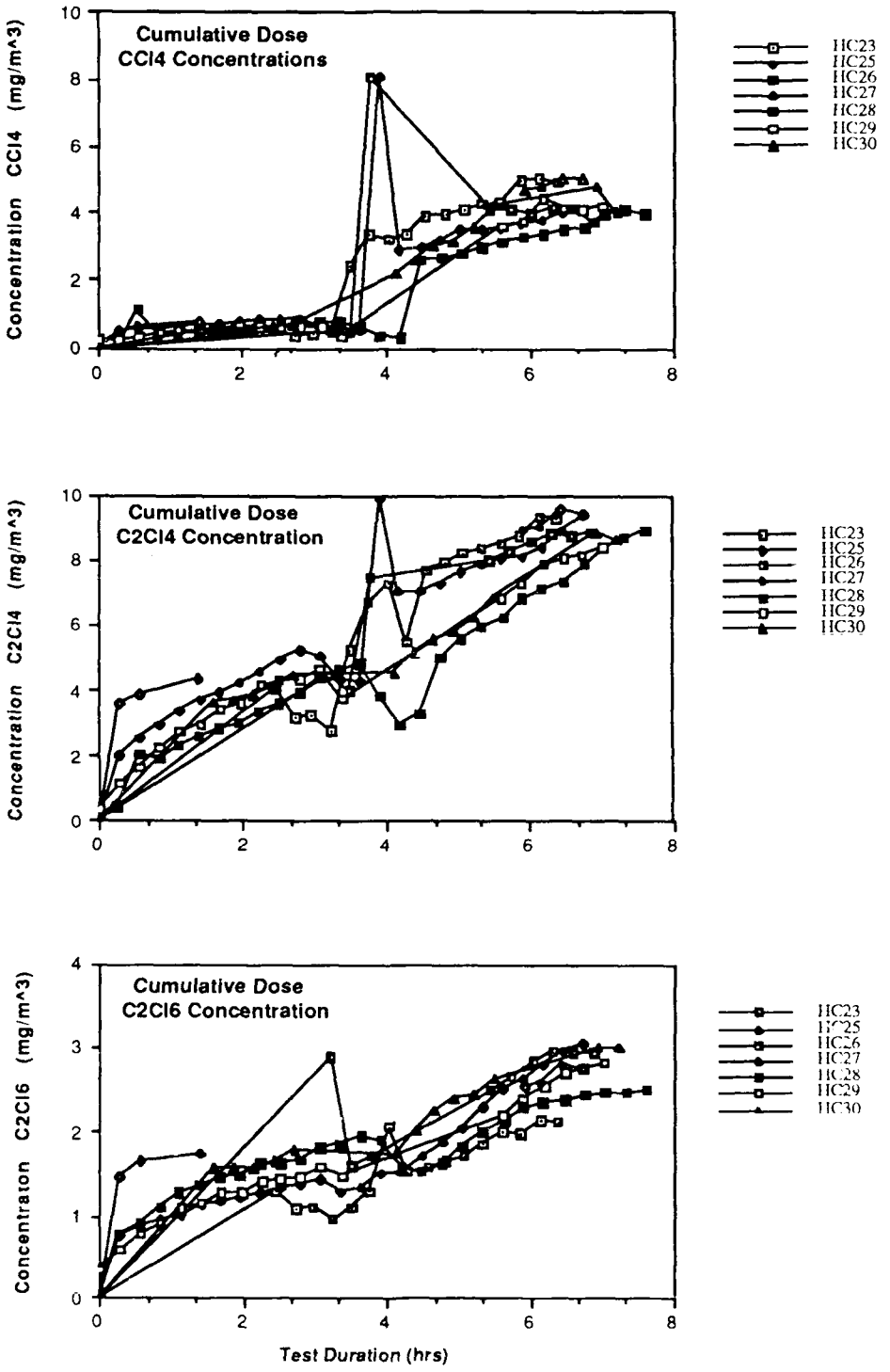


FIGURE 3.16. CONCENTRATION OF CHLOROCARBONS IN WIND TUNNEL TESTS SECTION DURING THE CUMULATIVE DOSE EXPERIMENTS

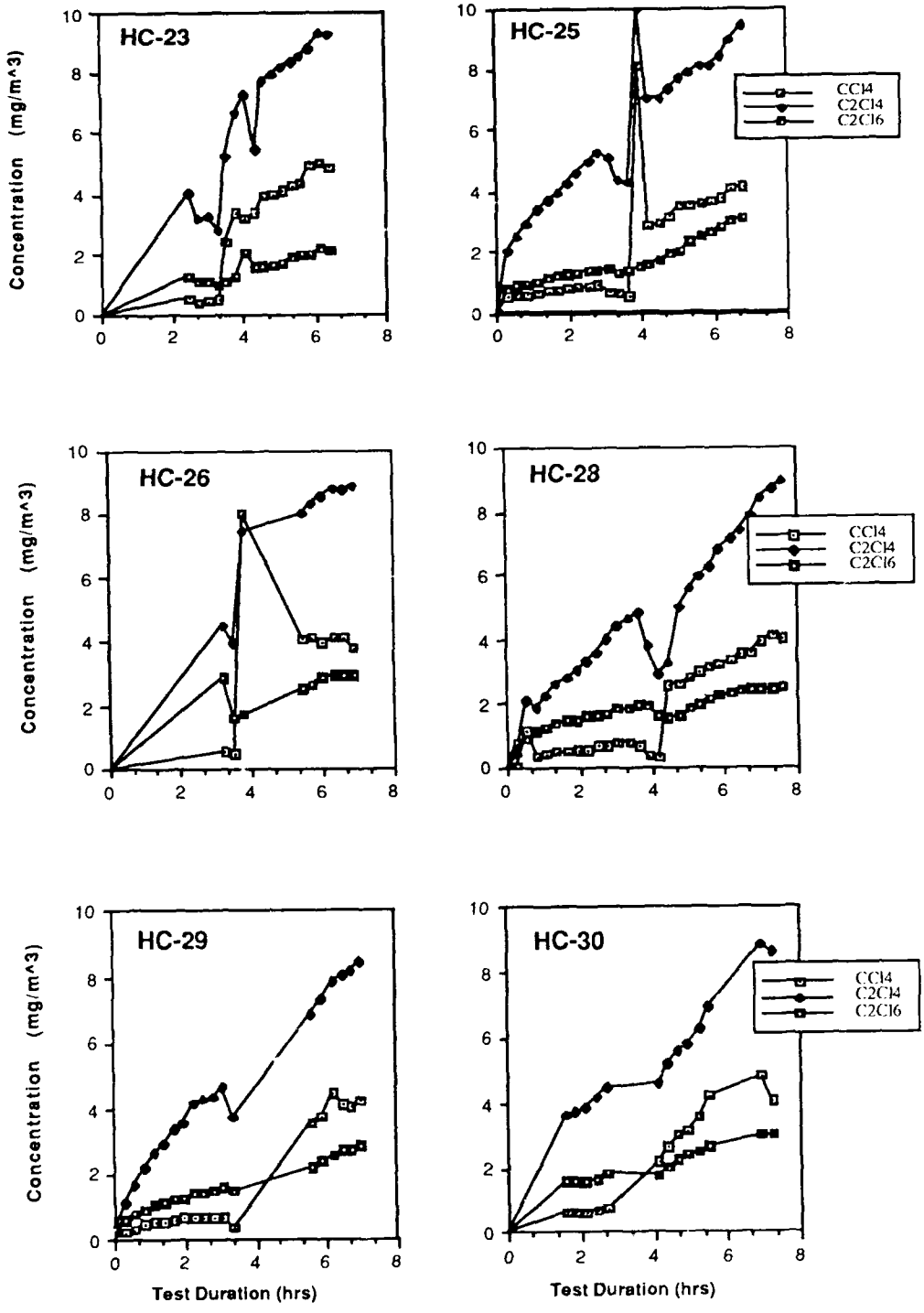


FIGURE 3.17. CONCENTRATION OF CHLOROCARBONS IN WIND TUNNEL TEST SECTIONS DURING INDIVIDUAL HC CUMULATIVE DOSE EXPERIMENTS

the pot size. It may be that when the larger pots are used, the mass of C_2Cl_4 produced per gram of material burned decreases. But because more material is burned per unit time, the result is that C_2Cl_4 is released at a similar net rate.

3.2.2 Inorganic Characterization of Aerosol

Aerosol Mass Filters. Aerosol and deposition filters were leached with either deionized water or 0.25 M HCl during early tests (HC-5). The water extracts were analyzed for metals by ICAP, and for Cl^- by IC; acidic extracts were analyzed for metals only. If a significant portion of the collected Zn on the filters was as the oxide, the recovery of Zn in the water extraction would have been depressed relative to that in the acidic. No such bias was observed. Total aerosol mass on all filters ranged from about 0.5 to 10 mg; blank filter acidic-leach contribution of Zn was significant for the lower masses, so the acidic leachates were adjusted for the appropriate blank level. Filters for subsequent studies were preleached with acid and water, followed by freeze-drying to minimize physical damage. Unrinsed filters were used for HC10 through HC-14, due to unavailability of prepared filters; results were corrected for average background contribution due to the unwashed filter.

Table 3.6 summarizes inorganic components of aerosol mass filter leachates for HC5-19. Determinations are based on aerosol wet weight (i.e., aerosol filters not desiccated before leaching). The moisture contents of the aerosols have been reported earlier (see Table 3.2). The remainder of the mass is attributed mainly to carbonaceous ash, plus traces of organic residues. Although the majority of aqueous leachates agreed with acidic leachates of aerosol mass filters, particular deviations were observed during tests HC10-14 on deposition filters, as will be discussed later in this section. In the above table, HC-8 filter F5 was not considered because of suspected analytical problem with the IC analysis. A series of aerosol filters were analyzed during HC-21, with results given in Table 3.7. These show a gradual increase in Cl/Zn ratio with increasing mass (i.e., increasing aerosol concentration in the wind tunnel), with a leveling at roughly 1.2.

Chemical Analysis of Cascade Impactors. Although cascade impactor data was collected throughout each test series, chemical analysis of the metal constituents was only performed during HC16-18. For each test, a cascade impactor series was taken, and half of each collection filter was leached with 0.01 M HNO^3, for analysis of the leachate by ICAP. Chloride analyses were not performed. Ignoring any deviation in accuracy of filter division into equal halves, Zn distribution by particle size (Table 3.8) shows the majority of particles in the 4th and 5th size fraction, or 1- to 2-μm range. This is in good agreement with mass distribution data presented in Section 3.1, and no evidence of altered distribution of Zn with

TABLE 3.6. AEROSOL MASS FILTER ANALYSIS, INORGANIC COMPONENTS

Test ID	Zn	Al	Cl	N[a] (Zn,Al,Cl)	% Mass as ZnCl2	Cl/Zn Ratio
	.....(mg/g).....					
Averaging both acid and H2O filter leachates for Zn:						
HC5	240±10	4.9±2.3	302±1.1	4,2,2	50±2	1.259
HC8	228±20	1.7±.9	296	4,2,1	47±4	1.298
HC9	235±22	3.5±2.1	288±11	4,2,2	49±5	1.227
HC10	42±12	ND[b]	52	2,0,1	8.8±.6	1.226
HC11	256±36	13.6	297±7	4,1,2	53±8	1.162
HC12	256±15	7.6	294±1	4,1,2	53±3	1.150
HC13	214±7	5.7	233±25	4,1,2	45±2	1.091
HC14	232±5	4.1	253±6	4,1,2	48±1	1.093
HC16	259±6	8.2±.1	307±17	4,2,2	54±1	1.182
HC17	224±14	6.3±.3	286±4	4,2,2	47±3	1.277
HC18	103±5	2.5±.1	127±1.9	4,2,2	22±1	1.231
HC19[c]	225±1	8.0	257	2,1,1	47±1	1.140
HC19[d]	134±6	3.6	163	2,1,1	28±1	1.216
HC20	284±32	7.4±1.0	ND	16,16,0	59±6	ND
Limited avg.[e]	241±20		281±25		50±4	1.20±.07
HC22A	270±19	6.1±1.4	315±28	4,4,2	56±4	1.126
HC23A	270±6	6.0±.8	311±5	4,2,2	56±1	1.142
HC24A	257±3	4.8±.5	291±4	3,3,2	54±1	1.132
HC25A	256±12	5.9±1.1	279±6	4,4,2	53±2	1.123
HC26A	278±11	5.1±.6	316±13	4,4,4	58±2	1.138
HC27A	274±7	5.8±.3	326±11	4,4,2	57±1	1.172
HC28A	267±2	4.4±0	297±10	2,2,2	56±0	1.113
HC29A	274±7	3.9±.3	316±1	4,4,2	57±1	1.145
HC30A	264±20	5.7±.6	298±18	4,4,4	55±4	1.129
A-Series Average	268±13	5.4±1.0	306±18	33,33,22	56±3	1.14±.02
HC22B	246±3	5.1±.1	280±5	4,4,2	51±1	1.149
HC23B	218±18	4.9±.2	243±16	4,4,2	46±4	1.198
HC24B	243±4	4.7±.4	282±2	4,4,2	51±1	1.176
HC25B	230±9	4.3±.3	259±6	4,4,2	48±2	1.165
HC26B	246±5	5.1±1	289±4	4,4,4	51±1	1.173
HC27B	233±11	5.7±.4	261±7	4,4,2	49±2	1.166
HC28B	219±23	4.0±1.1	258±26	4,4,4	46±5	1.177
HC29B	233±5	4.2±.4	281±10	4,4,3	49±1	1.199
HC30B	224±2	6.8±.4	254±32	4,4,4	47±0	1.134
B-Series Average	232±14	5.0±1.0	268±22	36,36,25	48±3	1.17±.06

(a) Number of analyses used in average determination for Zn, Al, and Cl, respectively; both aqueous and acidic extractions included for Zn determination, while Al includes only acidic, and Cl includes only aqueous extracts.
(b) Not determined.
(c) Filters collected prior to rainout.
(d) Filters collected during rainout.
(e) Limited average does not include HC10, HC18, or HC19[d].

TABLE 3.7. CHEMICAL ANALYSIS OF AEROSOL MASS AS STEADY-STATE CONDITIONS ARE ATTAINED IN HC-21

Filter Number	Time Elapsed (min)	Mass on Filter (mg)	Zn (µg/Filter)	Cl (µg/Filter)	Cl/Zn Ratio (mg/mg)	Mass as $ZnCl_2$ (%)
1	18	nd[a]	340	378	1.111	nd
2	37	5.44	537	624	1.162	21.3
3	54	4.50	936	1102	1.177	45.3
4	66	5.02	1120	1352	1.207	49.2
5	77	5.21	1190	1469	1.234	51.0
6	89	6.18	1280	1571	1.227	46.1
7	101	6.94	1440	1720	1.194	45.5
8	113	10.37	2360	2841	1.204	50.2
9	128	12.57	3290	4018	1.221	58.1

(a) Not determined.

TABLE 3.8. PARTICLE SIZE DISTRIBUTION OF HC AEROSOLS AS DETERMINED BY Zn CONTENT IN ANDERSEN CASCADE IMPACTOR STAGES

Stage	Particle size (µm)	HC16 20% RH[a]	HC17 55% RH	HC18 85% RH
		.....% Zn per stage /total Zn recovery		
0	9.3	0.59	0.66	0.65
1	5.9	1.01	1.47	1.51
2	4.0	1.40	2.02	2.99
3	2.8	7.95	9.13	19.24
4	1.8	31.7	37.8	45.4
5	0.87	50.5	45.0	29.0
6	0.53	0.64	3.67	1.16
7	0.35	0.25	0.13	0.05
8-Filter	<0.3	0.02	0.09	0.00

(a) RH, relative humidity.

particle size was observed. The expected increase in average particle size with increasing percent relative humidity (RH) from particle hydration is also observed.

Chemical Analysis of Aqueous Gas Scrubbers. Data on the aqueous impinger of "bubbler" samples taken during the HC tests has been used mainly as a monitor for

production of gaseous HCl, and for direct determination of aerosol Cl/Zn ratios. More direct quantitation of the aerosol concentration using scrubber data is not possible, due to the unreliable nature of the flow rate through the bubblers, attributed in part to buildup of smoke particulate in the frit. However, since calculation of deposition velocity to exposed soil surfaces requires the use of Cl^- rather than Zn aerosol concentration, corroborating determinations of the aerosol Cl^-/Zn ratio are preferred. Table 3.9 presents analytical data of aqueous aerosol scrubber solutions collected during HC tests.

3.3 MASS LOADING AND DEPOSITION VELOCITY TO RECEPTOR SURFACES

3.3.1 Deposition to Surrogate Surfaces

Deposition velocities were measured to plant, soil, and surrogate surfaces located within the wind tunnel test section during HC tests. Surrogate deposition coupons were used to provide relatively uniform surfaces for aerosol deposition for comparison with plant and soil deposition data. Surfaces used include suspended glass filters, glass and polystyrene petri dishes, and glass microscope slides. The 47-mm glass fiber deposition coupons served as a model for foliar deposition, while the dry static plates were used as model for deposition to soil. Deposition to soils is discussed in Section 3.3.3.

Deposition to Glass Fiber Filters. Glass fiber filters (47 mm) were suspended by inserting one edge of the filter into the radial loop of a spring hung from the exposure chamber ceiling into the aerosol flowpath to imitate a leaf canopy. In this manner, both surfaces of the filters would be available to deposition, with deposition to the upper surfaces also aided by gravitational force. Results of deposition filters for all HC tests are summarized in Table 3.10. Several samples were clouded by analytical problems attributed to incomplete extraction of the Zn, particularly in aqueous extracts from HC10-14, as noted in the table. Consequently, some of these analyses were not included in overall averages. The Cl/Zn ratio shows a positive bias at low mass loadings (see HC22-30, series A), partly attributed to small Cl^- bleed problems from the Waters Wisp autosamplers used in the IC analyses, which become more significant at lower sample Cl^- concentrations. Deposition velocity to suspended filters correlated fairly well ($R^2 = 0.96$) with wind speed for tests HC11-14 (Figure 3.18), when the deposition filter in HC14 which had blown perpendicular to the wind flow was deleted. That filter would have a significant amount of mass loading due to impaction, rather than deposition. No deposition filters were available for chemical analysis from HC26A and HC26B tests. Note that V_d calculations are based on total surface area, with no correction for the portion of the filter masked by the suspension spring (see Section 3.1.4). Correction for that area would amount to an increase of about 2% in the V_d values calculated.

TABLE 3.9. CHEMICAL ANALYSIS OF AQUEOUS IMPINGER TRAP SOLUTIONS FROM HC TESTS

Test ID	Impinger No.	Interval (min)	pH	Zn (mg/L)	Cl/Zn ratio (mg/mg)
HC8	2	14	5.57	3.8	1.23
HC8	3	20	5.48	3.8	1.18
HC9	1	5	5.46	2.04	1.09
HC10	1	70	6.53	10.8	1.20
HC11	1	64	5.63	9.1	1.14
HC12	1	61	4.91	27.6	1.17
HC13	1	55	4.92	35.8	1.16
HC14	1	59	4.99	25.7	1.17
HC16	2	50	4.99	21.5	1.15
HC16	4	53	6.19	5.3	1.11
HC17	1	54	4.68	24.7	1.22
HC17	4	54	4.42	104	1.23
HC18	2	59	4.62	52.1	1.23
HC18	3	58	4.97	12.2	1.15
HC19	2	58	4.62	64.7	1.19
HC19	3	58	4.83	28.3	1.10
HC23	A	80	4.7	65.8	1.18
HC24	A	80	4.76	123	1.18
HC25	A	102	4.99	25.0	1.16
HC26	A	81	5.05	24.6	1.08
HC27	A	80	5.02	32.4	1.12
HC28	A	80	5.30	16.5	1.09
HC29	A	80	5.92	10.2	1.03
HC30	A	80	5.03	51.4	1.13
HC23	B	80	4.45	131	1.21
HC24	B	79	4.71	69.8	1.20
HC25	B	94	5.05	41.7	1.14
HC26	B	80	4.84	28.4	1.14
HC27	B	82	5.01	32.3	1.10
HC28	B	80	5.08	22.1	1.11
HC29	B	80	4.96	55.0	1.14
HC30	B	110	4.72	60.3	1.20
A-series Average (N=8)					1.12±.06
B-series Average (N=8)					1.15±.04
Overall Average (N=32)					1.15±.05

TABLE 3.10. DEPOSITION FILTER ANALYSIS, INORGANIC COMPONENTS. ASSUMES BOTH SIDES OF FILTERS AVAILABLE FOR DEPOSITION. (Part 1 = mg/g analysis, for comparison with aerosol concentrations; Part 2 = $\mu g/cm^2$ for comparison with other deposition measurement)

Part 1

Test ID	Zn	Al	Cl	N[a]	% Mass	Cl/Zn Ratio	V_d[b]
	.....(mg/g).....			(Zn,Al,Cl)	as $ZnCl^2$	(mg/mg)	(cm/s x 10^3)
HC5	190±10	4.8±.6	432±30	4,2,2	40±2	2.23±.18	8.9±.8
HC9	236±8	2.6	252	2,1,1	49±3	1.05±.09	124±10
HC10[c]	272±3	9.2	360	2,1,1	57±1	1.32	35.8±6
HC11[c]	267±10	11.3	518	2,1,1	56±3	1.94	9.0±.2
HC12[c]	232±8	6.6	478	2,1,1	48±2	2.06	13.4±1.1
HC13[c]	244±3	5.4	438	2,1,1	51±1	1.80	18.4±3.5
HC14[c]	253±11	4.0	323	2,1,1	51±3	1.28	51.2;112[d]
HC16	199±35	7.5	208	2,1,1	42±1	1.05	10.4±0.8
HC17	224±4	6.6	301	2,1,1	47±1	1.34	10.6±0.6
HC18	283±4	7.8	350	2,1,1	59±1	1.24	14.6±0.9
HC19	254±8	8.0	319	2,1,1	53±1	1.26	12.8±0.4

Part 2

Test ID	Zn	Al	Cl	N[a]	Cl/Zn Ratio	V_d[b]
	.....($\mu g/cm^2$).....			(Zn,Al,Cl)	(mg/mg)	(cm/s x 10^3)
HC5	13.8±1.3	0.36±.03	30.5±1.7	4,2,2	2.23±.18	8.9±.8
HC9	7.9±.3	0.04	38.5	2,1,1	1.05±.09	124±10
HC10[c]	11.0±2.5	0.44	17.3	2,1,1	1.32	35.8±6
HC11[c]	4.3±.2	0.18	8.1	2,1,1	1.94	9.0±.2
HC12[c]	9.1±1.0	0.25	17.1	2,1,1	2.06	13.4±1.1
HC13[c]	12.0±2	0.21	14.9	2,1,1	1.80	18.4±3.5
HC14[c]	29;63[d]	0.47	38.3	2,1,1	1.28	51.2;112[d]
HC16	18±2	0.07	21.0	2,1,1	1.05	10.4±0.8
HC17	21±1	0.22	26.7	2,1,1	1.34	10.6±0.6
HC18	25.2±2.1	0.09	29.8	2,1,1	1.24	14.6±0.9
HC19	25.8±1.1	1.05	32.3	2,1,1	1.26	12.8±0.4
HC22A	2.3	0.12	3.1	2,2,1	1.36	6.0
HC23A	2.1	0.11	2.8	2,2,1	1.51	4.0
HC24A	2.0	0.05	2.8	2,2,1	1.49	4.2
HC25A	2.3	0.07	2.9	2,2,1	1.31	5.1
HC27A	2.7	0.08	3.6	2,2,2	1.32	5.8
HC28A	2.4	0.05	3.1	2,2,2	1.26	4.8
HC29A	2.1	0.02	3.2	2,2,2	1.50	4.5
HC30A	2.6	0.10	3.5	2,2,2	1.32	5.8

TABLE 3.10. (Cont.)

HC22B	17.6	.45	22.0	2,2,1	1.18	9.0
HC23B	14.2	.37	17.5	2,2,1	1.22	8.0
HC24B	14.0	.32	15.4	2,2,1	1.20	8.1
HC25B	14.2	.28	16.9	2,2,1	1.19	8.8
HC27B	13.8	.39	16.6	2,2,2	1.20	8.6
HC28B	13.7	.32	16.5	2,2,2	1.21	8.5
HC29B	14.0	.25	16.9	2,2,2	1.21	8.2
HC30B	13.5	.42	16.4	2,2,2	1.22	8.3
AVERAGE						
A-series	2.3±.3	.08±.03	3.2±.3	16,16,12	1.37±.11	5.0±.8
B-series	14.3±1.4	.35±.07	17.1±.02	16,16,12	1.21±.01	8.4±.5
Overall, partial (not including HC5-14)				20	1.23±.26	

(a) Number of analyses used in average determination for Zn, Al, and Cl, respectively; both aqueous and acidic extractions included for Zn determination, except as noted by (c), while Al includes only acidic, and Cl includes only aqueous extracts.

(b) Deposition velocities determined by compari 'n mass in aerosol vs. deposition results.

(c) Only acidic extraction results are included for ⁄ letermination, since incomplete extraction was suspected for the water extractions.

(d) The wide variation in deposition velocities due to the bias introduced when some filters bent in the higher wind speeds, causing a greater degree of deposition by impaction. The higher Zn and V_d value listed is from a filter biased in such a manner.

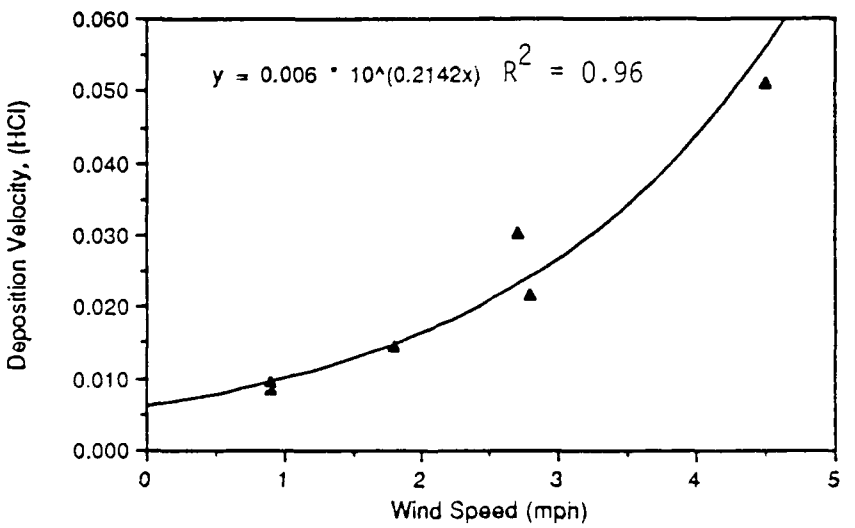


FIGURE 3.18. DEPOSITION VELOCITY ON GLASS FIBER SURFACES VS. WIND SPEED (HC11-14)

Deposition onto Wet and Dry Static Surfaces. Wet and dry deposition coupons were included in most of the HC exposures, to provide deposition rate data as well as for chemical analysis. Although the deposition velocities provided in Tables 3.11 through 3.13 are calculated based on aerosol Zn concentration as determined from the aerosol mass filters, calculation based on aerosol chloride concentrations were equally consistent (Table 3.I4). The pH of aqueous leachate samples was monitored, as an indication of

TABLE 3.11. DRY DEPOSITION PLATES EXPOSED DURING HC TESTS

Test ID	Zn	Al	Cl	N[a] (Zn,Al,Cl)	Cl/Zn Ratio (mg/mg)	V_d[b] (cm/s x 10^3)
	.....($\mu g/cm^2$).....					
HC8	10.8±.1	0.07±.02	13.4±.4	10,10,5	1.18±.02	21.0±0.6
HC9	8±0	0.06±.02	9	4,2,1	1.08	23.2±0.7
HC11	8±0	0.17±.04	9±0	6,6,2	1.09±.07	17.1±0.0
HC12	18±4	0.31±.04	23±1	6,6,2	1.14±.03	30.0±0.4
HC13	8±1	0.14±.01	9±0	6,6,2	1.09±.05	12.6±0.0
HC14	8±1	0.12±.01	9±0	6,6,2	1.09±.05	14.3±0.9
HC16	23±2	0.57±.05	29±2	4,4,2	1.23±.01	13.5±0.9
HC17	38±1	1.02±.02	48±0	4,4,2	1.23±.01	18.9±0.4
HC18	47±2	1.20±.05	59±0	4,4,2	1.21±.02	27.3±1.2
HC19(c)	40±1	1.21±.04(d)	50±1	4,2,2	1.26±.02	19.8±0.3
HC19(e)	124±19	ND	180±33	3,0,3	1.45±.05	61.3±0.9
HC20	62±1	1.50±.07	74±1	4,4,2	1.19±.03	35.7±0.7
HC22A	4.4±.3	0.08±.01(d)	4.8±.3	4,2,4	1.10±.01	11.7±0.9
HC23A	5.6±.5	0.10±.01(d)	6.0±.6	4,2,4	1.08±.03	10.8±0.9
HC24A	6.2±.7	0.10±.02	7.3±.8	4,4,4	1.10±.02	14.3±1.5
HC25A	7.3±1.3	0.14±.03	8.1±1.5	4,4,4	1.11±.02	16.1±2.9
HC26A	6.2±.6	0.09±.02	6.6±.6	4,4,4	1.08±.02	13.2±1.3
HC27A	8.2±1.2	0.15±.03	9.5±1.4	4,4,4	1.16±.00	17.8±2.6
HC28A	8.2±2.4	0.12±.04	9.3±2.8	4,4,4	1.14±.06	15.7±4.6
HC29A	5.4±0.3	0.09±.01(d)	5.9±.5	4,2,4	1.08±.08	11.6±0.7
HC30A	6.9±2.1	0.11±.01(d)	8.5±4.3	4,2,4	1.19±.02	14.9±4.6
HC22B	35.8±1.5	0.66±.02	41.9±1.2	4,4,4	1.17±.03	18.3±0.8
HC23B	35.8±.4	0.75±.02	41.0±1.0	4,4,4	1.14±.02	20.2±0.2
HC24B	30.0±.4	0.56±.01	35.8±.2	4,4,4	1.19±.01	17.5±0.2
HC25B	31.3±2.3	0.56±.04	38.7±1.4	4,4,3	1.20±.01	19.3±1.4
HC26B	37.9±1.2	0.79±.02	45.7±1.6	4,4,4	1.20±.01	22.1±0.7
HC27B	31.4±.9	0.76±.03	38.4±1.3	4,4,4	1.22±.01	19.7±0.5
HC28B	29.9±1.2	0.45±.05	35.8±.5	4,4,4	1.20±.01	18.6±0.7
HC29B	34.7±1.6	0.64±.07	41.1±2.5	4,4,4	1.18±.02	20.2±0.9
HC30B	33.7±1.4	0.99±.05	42.0±1.8	4,4,4	1.25±.02	20.8±0.9

TABLE 3.11 (Cont.)

AVERAGES						
A-series	6.5±1.7	0.12±.03	7.3±2.3	36	1.12±.08	14.0±3.2
B-series	33.4±3.0	0.70±.15	40.1±3.4	36,35	1.20±.03	19.6±1.5
Overall				30	1.17±.08	

(a) N = number of analyses used in average determination for Zn, Al, and Cl, respectively; both aqueous and acidic extractions included for Zn and Al determination, except as noted by (d), while Cl includes only aqueous extracts.
(b) Deposition velocities determined by comparing mass of Zn in aerosol vs deposition results.
(c) Deposition plates taken upwind of simulated rainfall incident.
(d) Only acidic leachate analyses included; aqueous-leached plates lost Al prior to analysis.
(e) Deposition dishes placed within simulated rainfall region, and so would also include aerosol washout as well as washoff from nearby plants.

TABLE 3.12. DRY DEPOSITION NO-WALLED SURFACES (MICROSCOPE SLIDES) EXPOSED DURING HC22-30 TESTS, SERIES A AND B

Test ID	Zn	Al	Cl	N(a)	Cl/Zn Ratio	V_d(b)
	.....	($\mu g/cm^2$).....		(Zn,Al,Cl)	(mg/mg)	(cm/s x 10^3)
HC22A	3.3±.1	.09±.00(d)	4.3±.1	4,2,2	1.33	8.8±0.3
HC23A	3.6±.4	.07±.00(d)	4.5±.1	4,2,2	1.24	7.0±0.2
HC24A	5.5±.5	.10±.01(d)	6.5±.4	4,2,2	1.23	11.8±1.0
HC25A	3.6±.1	.09±.00(d)	4.4±.1	4,2,2	1.26	7.8±0.2
HC26A	3.5±.1	.07±.00(d)	4.3±.1	4,2,2	1.27	7.4±0.3
HC27A	3.5±.1	.08±.00(d)	4.3±.0	4,2,2	1.23	7.7±0.1
HC28A	4.2±.1	.09±.00(d)	4.3±.0	4,2,2	1.05	8.1±0.1
HC29A	3.3±.1	.05±.01(d)	4.0±.1	4,2,2	1.22	7.1±0.2
HC30A	3.5±.1	.08±.01(d)	4.2±.0	4,2,2	1.23	7.6±0.2
HC22B	30.5±.4	.58±.00(d)	35.9±.3	4,2,2	1.17	15.6±0.2
HC23B	30.3±.1	.66±.01(d)	35.0±.2	4,2,2	1.16	17.1±0.1
HC24B	26.1±.3	.45±.01	31.2±.3	4,4,2	1.18	15.2±0.2
HC25B	25.8±.2	.44±.02	30.4±.0	4,4,2	1.18	15.9±0.2
HC26B	26.5±.3	.51±.04	30.8±.4	4,4,2	1.16	15.4±0.1
HC27B	25.8±.1	.59±.03	31.1±.2	4,4,2	1.21	16.2±0.1
HC28B	25.9±.2	.43±.04	30.3±.4	4,4,2	1.17	16.1±0.1
HC29B	26.5±.2	.49±.00(d)	30.9±.3	4,2,2	1.17	15.5±0.1
HC30B	25.4±.3	.70±.07	31.0±.3	4,4,2	1.22	15.7±0.2
AVERAGES						
A-series	3.8±7	.08±.02	4.5±.9	36,18,19	1.21±12	8.1±1.4
B-series	27.0±1.9	.56±.1	31.8±2.0	36,18,18	1.18±.02	15.9±.6
Overall				18	1.20±.06	

(a) N = number of analyses used in average determination for Zn, Al, and Cl, respectively; both aqueous and acidic extractions included for Zn and Al determination, except as noted by (d), while Cl includes only aqueous extracts.
(b) Deposition velocities determined by comparing mass of Zn in aerosol vs deposition results.
(c) Deposition plates taken upwind of simulated rainfall incident.
(d) Only acidic leachate analyses included; aqueous-leached plates lost Al prior to analysis.

TABLE 3.13. WET DEPOSITION PLATES EXPOSED DURING HC TESTS

Test ID	Zn	Al	Cl	N[a]	Cl/Zn Ratio	V_d[b]
	.....($\mu g/cm^2$).....			(all)	(mg/mg)	(cm/s x 10^3)
HC8	23±1	0.17±.02	28±1	6	1.23	43.5
HC9	12	0.08	14	2	1.14	35.5
HC11	15	0.34	19	2	1.22	32.6
HC12	22	0.40±.05	25±3	2	1.15	32.2
HC13	13	0.25	15	2	1.18	19.2
HC14	9±2	0.15±.04	12±4	2	1.38	15.4
HC16	27	0.72	36	2	1.32	15.7
HC17	63	1.69	80	2	1.26	31.4
HC18	72	1.87	88	2	1.23	41.4
HC19	83±15	2.5±.4	109±20	2	1.32	41.1
HC20	79±3	2.1±.1	105	2	1.33	45.7
HC22A	8.3	0.15	9.6	2	1.16	22.1
HC23A	8.0	0.14	9.4	2	1.17	15.6
HC24A	8.3	.14	.9.5	2	1.15	17.9
HC25A	7.3	.15	8.6	2	1.18	16.1
HC26A	9.6	.16	10.8	2	1.13	20.6
HC27A	8.3	.16	9.8	2	1.19	18.0
HC28A	8.7	.14	10.1	2	1.16	16.8
HC29A	7.7	.14	9.1	2	1.17	16.6
HC30A	8.3	.16	9.5	2	1.14	17.9
HC22B	57.0	1.14	67.2	2	1.18	29.1
HC23B	56.5	1.24	66.8	2	1.18	31.8
HC24B	46.8	.89	57.5	2	1.23	27.3
HC25B	45.3	.85	55.8	2	1.23	27.9
HC26B	45.3	.97	56.2	2	1.24	26.4
HC27B	49.5	1 21	59.8	2	1.21	31.0
HC28B	49.5	.90	60.2	2	1.22	30.8
HC29B	48.3	.94	58.2	2	1.21	28.2
HC30B	46.9	1.41	58.4	2	1.25	28.9
AVERAGES						
A-series	8.3±.7	.15±.01	9.6±.7	18	1.16±.02	17.9±2.1
B-series	49.4±4.4	1.06±.19	60.0±4.2	18	1.22±.02	29.0±1.9
Overall Average			29	1.21±.06		

(a) N = number of analyses used in average determination for Zn, Al, and Cl; only aqueous plates exposed, so Al values are not considered reliable. When replicate analyses are similar, no standard deviation is listed: when replicate analyses diverge, standard deviations are given to show range of uncertainty.

(b) Deposition velocities determined by comparing mass of Zn in aerosol vs deposition results.

TABLE 3.14. COMPARISON OF DEPOSITION VELOCITIES CALCULATED BASED ON ZN AEROSOL CONCENTRATIONS TO THOSE CALCULATED BASED ON Cl^- AEROSOL CONCENTRATIONS

	WET DEPOSITION PLATES			DRY DEPOSITION PLATES/SURFACES		
TEST ID	V_d vs Zn	V_d vs. Cl	N[a]	V_d vs Zn	V_d vs. Cl	N
	... ($x10^{-3}$ cm/s).....			.... ($x10^{-3}$ cm/s).....		
HC22-30A						
petri	17.9±2.1	18.2±1.9	18	14.0±3.2	13.8±4.1	36
glass slides				8.1±1.4	8.6±1.9	36,19
dep filters				5.0±.8	6.0±.7	16,12
HC22-30B						
petri	29.0±1.9	30.7±2.2	18	19.6±1.5	20.5±1.8	36,35
glass slides				15.9±.6	16.3±.9	36,18
dep filters				8.4±.5	8.8±.6	16.12

(a) N = number of analyses; where more than one number listed, first is number of analyses based on Zn and second is number of analyses based on Cl^-.

possible acid formation during HC combustion. Deposition velocity from the other 4.5 m/s test (HC-9) is also elevated. The surface area of the short walls of the petri plate covers is not included in the area used for calculating Vd.

Deposition velocities to dry petri plates did not correlate well with wind speed (HC11-14); Vd on wet plates showed inverse correlation (Y = .042 * 10^(0.1001*X), R^2 = 0.90), but the type of curve fit may not be significant, since the linear fit was not too bad either (R^2 = 0.86), with only 4 data points. Increased humidity resulted in the expected increased deposition for wet and dry plates. Average deposition velocity to wet surfaces was twice that to dry surfaces for HC8. However, the ratio fluctuated in later tests ranging from under 1.3 (HC12, HC14, HC16, and HC20), through several data at about 1.5-1.6 (HC13, HC17, and HC18), to 2 (HC11 and HC19). During the cumulative dose tests, ratio of wet deposition to dry deposition was 1.3 for A-series, and 1.5 for B-series. The ratio was not well correlated with wind speed, but did increase with increasing relative humidity. Deposition velocities for dry plates averaged 0.019 cm/s over the series HC11 to HC17 covering moderate humidity levels (60%, Table 3.11), while wet deposition plates averaged 0.026cm/s over the same test group (Table 3.13).

3.3.2 Comparison of Deposition Surfaces.

Deposition velocities calculated from the static deposition plates (Table 3.11 through 3.13) did not match well with those determined by suspended deposition filters (Table 3.10). Some of these differences were anticipated, since some degree of turbulence was associated with the plate lip (8 mm on polystyrene petri covers; 13 mm on glass petri covers). In addition, equal deposition was assumed on both sides of the suspended filter, when in fact equal deposition did not occur, and these data were averages of a surface with both top and bottom exposed to the aerosol (to simulate a plant leaf). At low wind speed (HC11), V_d on dry deposition plates was about twice that measured on the deposition filters. As wind speed increased (HC11 to HC14), the ratio of V_d on dry static plates to that on deposition filters decreased approximately from 2.1 to about 1.26, at least in part due to an increased role of impaction as a mechanism of particle deposition to the suspended filter coupons: with increasing wind speed, filters directly in the wind path tended to bend, causing increased deposition from impaction. With increasing humidity (HC16 to HC18), the ratio of V_d on dry static plates to that on deposition filters increased slightly from 1.3 to 1.5 (ignoring rainout), while the ratio of V_d on wet surfaces to that on dry static plates increased to about 2.

3.3.3 Mass Loading and Deposition Velocities for Inorganics to Soil Surfaces

Soil thin lens exposure conditions are detailed in Section 2.5, and effects of these exposures are given in Section 3.4. Although change in humidity caused an increase in aerosol deposition, the increase was less than 30%, based on Cl^- values for both soils. Chloride must be used for any estimates of deposition, since the solubility of Zn showed great dependence on soil type exposed. Chloride concentrations in the aerosol are determined from the aerosol filter leachate data (see Table 3.6), which is limited to two Cl^- determinations per test. To verify the validity of using this estimate, some comparisons were first made using the ratio of Cl^- to Zn found on the various different sampling mechanisms (see Tables 3.6 to 3.13 and Table 3.15). Bubbler Cl/Zn ratios closely resembled those found for the aerosol mass filter leachates; we chose to use aerosol filter data for estimation of average aerosol Cl^- content when calculating deposition to soils, since the data set was more complete, and was directly linked to the determination of aerosol Zn concentrations. Deposition velocities so calculated are shown in Table 3.16. These deposition velocities more closely resemble deposition velocities observed to wet petri plates (Table 3.13), with the exception of HC16, where the soil deposition results nearly doubled the corresponding wet deposition results. However, the HC16 wet deposition results themselves showed unusually small increase over the dry deposition determinations, tentatively ascribed to result from the very low relative humidity (20%), but

not adequately explained. Although change in humidity caused an increase in aerosol deposition, the increase was less than 25%, based on Cl^- values for Burbank and Maxey Flats soils.

TABLE 3.15. SUMMARY OF SELECTED CHLORIDE/ZINC RATIOS DETERMINED FROM DEPOSITION AND AEROSOL SAMPLING METHODS. FOR ALL LISTED, N=2 UNLESS OTHERWISE SPECIFIED AS (N).

Test I D	Impinger Mass Filt.	Aerosol Wet Plate	Deposition Dry Plate	Deposition Filter HC16	Deposition
	1.13	1.20	1.33	1.26	1.27 (1)
HC17	1.22	1.21	1.27	1.26	1.32 (1)
HC18	1.19	1.18	1.22	1.26	1.25 (1)
HC19	1.15	1.15	1.31	1.25	1.22 (1)
HC22A	1.12±.06(8)	1.14±.02(22)	1.16±.02(18)	1.12±.08(36)	1.37±.11(12)
HC22B	1.15±.04(8)	1.17±.06(25)	1.22±.02(18)	1.20±.03(35)	1.21±.01(12)

TABLE 3.16. DEPOSITION VELOCITIES TO SOILS EXPOSED DURING RELATIVE HUMIDITY TESTS (HC16-19) AND ONE LOW (HC22A) AND HIGH (HC22B) AEROSOL CONCENTRATION EXPOSURE OF THE CUMULATIVE DOSE SERIES; BASED ON Cl- CONTENT IN THE AEROSOL, AS DETERMINED BY AEROSOL FILTER LEACHATES

Soil Type	Test ID	N	Total Cl^-	Control Cl^-	Added Cl^-	V_d (cm/s x 10^3)
			.....(µg/mL extractant).....			
Burbank	HC16	2	94.2	0.13	94.1	27.8
	HC17	5	99.4±1.7	0.13	99.2	23.3±0.4
	HC18	2	120.5	0.13	120.4	34.2
	HC19	2	110.4	0.13	110.3	28.4
	HC22A	2	9.3	0.2	9.1	13.5
	HC22B	2	77.2	0.2	77.0	22.5
Maxey Fl.	HC16	2	107.4	0.44	107.0	31.6
	HC17	5	106.4±2.3	0.44	106.0	24.9±0.6
	HC18	2	136.0	0.44	135.5	38.6
	HC19	2	115.8	0.44	115.3	29.6
	HC22A	2	10.4	0.4	10.0	14.8
	HC22B	2	90.5	0.4	90.1	26.3
Ritzville	HC17	3	104.1±1.2	0.11	104.0	24.5±0.3
Quillayute	HC17	3	111.8±3.3	2.4	109.4	25.8±0.8
Shawano	HC17	3	107.9±4.2	1.0	106.9	25.2±1.0
Yamac	HC17	3	141.9±2.5	27.4	114.5	26.9±0.6
All soils	HC16-17	26		Average values	24.9±1.3	
B+M[a]	HC18	4		Average values	36.4±2.5	
B+M	HC19	4		Average values	29.0±0.9	
B+M	HC22A	4		Average values	14.1±1.2	
B+M	HC22B	4		Average values	24.4±1.2	

(a) Burbank and Maxey Flats only.

3.3.4 Interaction of HC Smokes with Soils

A primary goal in these studies is to observe the effects on soils covering a wide range in soil properties such as might be found under actual field conditions. Therefore, emphasis was placed on the diversity of soils rather than on the statistical response of a single soil to the aerosol stress. Six soils covering a range of physical and chemical properties were exposed to HC aerosol deposition. Two of these soils (Burbank and Maxey Flats; see Table 2.5) were exposed during all relative humidity runs, while the other four soils were exposed during the midrange humidity test only. Palouse was not included in soil lens exposures, but was included in microbial studies. Following exposure, the soils were leached with deionized water, as described in Section 2.5.2, with periodic subsamples taken for analysis of elemental composition, anion distribution, and dissolved organic and inorganic carbon levels.

Leaching studies were performed to detect alteration of normal soluble species from aerosol exposure. Anion/cation balance is a dimensionless factor defined as the difference between total cations and anions, divided by the sum of the ionic species, on an equivalence basis. It is used as an indicator of the relative efficiency in analyzing all the major controlling species in solution. While the dependence on total ion concentration of the solution serves to normalize the results somewhat to concentration, very weak ionic strength solutions show poorer balance due to the increased deviation on low concentrations of individual analytes, as well as variations due to trace carryover in some analytical methods (specifically, an autosampler). The balance is often upset in surface soils by the presence of organic ions such as organic acids, which both interfere with analyses and also account for some of the anion imbalance. A major ion is often bicarbonate, as is observed in Maxey Flats. Determination of inorganic carbon was performed routinely by calculating the difference between dissolved total carbon and organic carbon (DOC) (following acidification and sparging), with only intermittent direct determination of inorganic carbon. Consequently, presence of any purgable organics is included in the inorganic carbon value. Because not all samples were analyzed directly for inorganic carbon and the resultant indirect determination of DOC including purgable organics, values for DOC listed in the tables are for the direct determination only. Comparisons drawn between control and exposed soils are still valid, since all data are treated similarly.

Evaporation was estimated at 0.394±016 g/day (N=2) for the 100 mL/10 g soil extracts, and 0.533±.044 g/day (N=12) for the 20 g/200 mL soil extracts. Evaporation losses to the pots were not replaced. Thus, a 15-day period should result in concentration by about 4% and 6% for the 20-g and 10-g extracts, respectively.

Different soil types do have markedly different responses to the deposited-aerosol stress. The concentration of added aerosol appears to be best reflected in the chloride concentrations, adjusted for control soluble concentrations: soluble Zn levels from exposed soils range from 1µg/g Yamac soil to more than 400 µg/g Maxey Flats soil (Figure 3.19), while added-chloride values cluster around 1100 µg/g for all soils. These results point out why water- or weak acid (0.01 M HNO_3) -extracted Zn cannot be used for determination of deposition velocities on soils.

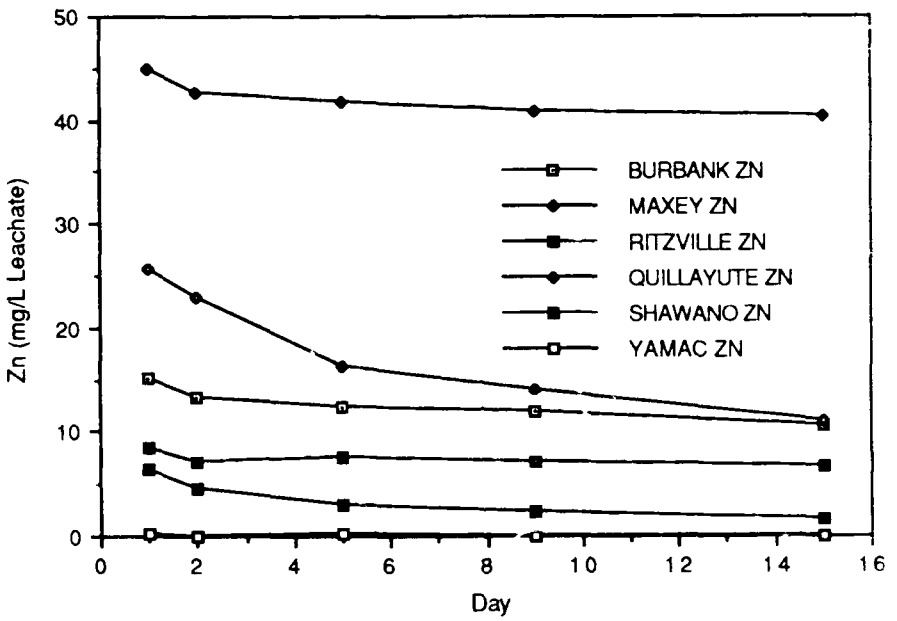


FIGURE 3.19. SOLUBLE ZN LEVELS IN 1:10 SOIL: WATER EXTRACTS OF HC-EXPOSED SOILS WITH TIME

Results of Soil Exposures. Analytes in Burbank and Maxey Flats exposed soil extractions showed that changes relative to the controls are listed in Table 3.17 and Table 3.18, respectively. Included in these tables is an analysis of overall mean and standard deviation for duplicate soils exposed in each of the relative humidity tests, as a means of estimating variability due to humidity and any corresponding change in deposition. A major controlling ion for anion-cation balance is often bicarbonate. In Maxey Flats, for example, a high bicarbonate determination (by difference) resulted in an abnormally high negative ion balance in 9-day control (Table 3.18). All other ion balances listed are reasonable.

TABLE 3.17. COMPARISON OF SOLUBLE SPECIES FROM CONTROL AND EXPOSED BURBANK SOIL

TEST	LEACH DAY NO.	REPS (N)	FUNCTION	PH	DOC [.1](a)	NO3- [.05]	PO4- [.1]	SO4= [.1]	CL- [.03]	ZN [.02]	MG [.06]	CA [.01]	K [.3]	NA [.01]	MN [.002]	SR [.002]	BALANCE DIFF/SUM
CONTROL	1	2	AVERAGE	7.84	5.3	0.8	1.5	0.9	0.13	0.04	0.7	3.5	9.6	0.3	0.003	0.014	-0.024
CONTROL	2	1		7.87	4.8	1.0	1.6	0.9	0.18		0.9	4.5	10.2	0.2		0.017	-0.080
CONTROL	5	2	AVERAGE	7.85	5.3	2.7	1.9	0.8	0.19	0.03	1.2	5.9	11.8	0.3	0.004	0.023	0.020
CONTROL	9	1		7.91	4.9	4.2	1.9	1.0	0.15		1.3	6.4	12.0	0.3		0.024	-0.056
CONTROL	15	1		8.01	5.1	4.9	2.0	1.1	0.18		1.5	7.0	12.5	0.3		0.027	0.044
CONTROL	1 TO 15	7	AVERAGE	7.89	5.1	2.7	1.8	0.9	0.17	0.03	1.1	5.2	11.0	0.3	0.003	0.020	-0.019
CONTROL	1 TO 15	7	STD DEV	(±0.07)	(±0.3)	(±1.6)	(±0.2)	(±0.1)	(±0.03)	(±0.02)	(±0.31)	(±1.42)	(±1.3)	(±0.1)	(±0.002)	(±0.005)	(±0.052)
EXPOSED:																	
HC16	1	2	AVERAGE	6.23	7.9	0.6	0.4	1.5	94.80	11.10	6.2	29.1	19.6	0.5	0.190	0.132	0.015
HC17	1	5	AVERAGE	6.36	7.9	0.6	0.2	1.9	100.02	15.04	6.4	31.0	19.4	0.5	0.194	0.138	0.028
HC17	1	5	STD DEV	(±0.05)	(±0.5)	(±0.0)	(±0.0)	(±0.2)	(±1.13)	(±1.33)	(±0.11)	(±0.51)	(±0.6)	(±0.1)	(±0.021)	(±0.003)	(±0.013)
HC18	1	2	AVERAGE	6.09	9.6	0.5	0.2	1.0	120.50	22.30	7.0	34.6	20.2	0.5	0.244	0.154	-0.003
HC19	1	2	AVERAGE	6.45	9.7	0.6	0.2	1.1	110.40	20.05	6.9	33.1	20.5	0.4	0.221	0.150	0.020
HC16-19	1	11	AVERAGE	6.30	8.0	0.6	0.2	1.4	104.30	15.46	6.1	29.6	18.5	0.4	0.195	0.133	0.015
HC16-19	1	11	STD DEV	(±0.14)	(±2.3)	(±0.0)	(±0.1)	(±0.4)	(±9.70)	(±5.66)	(±1.70)	(±8.29)	(±5.0)	(±0.1)	(±0.054)	(±0.037)	(±0.013)
HC17	2	1		6.44	6.2	0.6	0.2	1.8	100.70	13.40	6.5	31.0	20.0	0.4	0.202	0.140	0.013
HC16	5	2	AVERAGE	6.36	6.0	0.6	0.4	1.4	95.80	9.12	6.6	31.0	20.9	0.4	0.276	0.142	0.014
HC17	5	5	AVERAGE	6.24	6.1	0.6	0.2	1.8	103.46	12.30	6.7	32.0	20.5	0.5	0.251	0.144	0.007
HC17	5	5	STD DEV	(±0.10)	(±0.2)	(±0.1)	(±0.0)	(±0.3)	(±2.35)	(±1.11)	(±0.20)	(±1.06)	(±0.5)	(±0.0)	(±0.016)	(±0.005)	(±0.011)
HC18	5	2	AVERAGE	6.29	8.2	0.6	0.2	1.2	121.45	19.25	7.6	36.5	21.6	0.6	0.394	0.169	0.006
HC19	5	2	AVERAGE	6.69	6.9	0.5	0.2	1.2	112.48	16.75	7.3	34.7	19.7	0.5	0.303	0.161	0.008
HC16-19	5	11	AVERAGE	6.35	7.0	0.6	0.3	1.4	107.30	13.79	7.0	33.1	20.6	0.5	0.291	0.151	0.009
HC16-19	5	11	STD DEV	(±0.19)	(±2.0)	(±0.0)	(±0.1)	(±0.3)	(±9.26)	(±3.71)	(±0.42)	(±2.19)	(±0.8)	(±0.1)	(±0.056)	(±0.012)	(±0.003)
HC17	9	1		6.37	6.3	0.6	0.3	1.9	102.40	11.90	7.0	32.3	20.8	0.5	0.262	0.149	0.016
HC17	15	1		6.29	5.9	0.6	0.3	2.0	104.84	10.50	7.2	33.7	20.5	0.5	0.264	0.156	0.023
HC16-19	OVERALL	25	AVERAGE	6.33	7.4	0.6	0.3	1.5	105.41	14.79	6.8	32.4	20.2	0.5	0.248	0.147	0.013
HC16-19	OVERALL	25	STD DEV	(±0.15)	(±1.3)	(±0.0)	(±0.1)	(±0.4)	(±8.87)	(±3.99)	(±0.42)	(±2.07)	(±0.8)	(±0.0)	(±0.057)	(±0.011)	(±0.009)
HC22A	1	2	AVERAGE	7.51	6.1	0.8	1.1	1.4	9.27	0.02	1.2	5.6	11.9	0.3	0.004	0.023	0.047
HC22A	5	2	AVERAGE	7.81	5.5	1.8	1.3	1.1	8.76	0.04	1.7	7.7	12.0	0.3	0.012	0.030	0.039
HC22B	1	2	AVERAGE	5.87	9.0	0.6	0.3	1.9	77.15	6.34	5.5	24.4	19.1	0.4	0.164	0.111	0.025
HC22B	5	2	AVERAGE	6.49	6.9	0.6	0.3	1.5	76.15	5.47	5.8	25.6	18.1	0.5	0.197	0.115	0.035
ACIDIFIED (+HCL)	CONTROL 5	1		6.66	4.8	4.04	2.0	1.01	44.030		3.04	14.5	16.5	0.41		0.061	-0.028
	10	1		6.74	7.0	5.14	1.6	1.23	42.160		3.46	16.3	17.7	0.46	0.008	0.069	0.040

(a) estimated detection limits, µg/mL; table values are in terms of µg/mL in the extraction solution (1:10 ratio of soil:water)

TABLE 3.18. COMPARISON OF SOLUBLE SPECIES FROM CONTROL AND EXPOSED MAXEY FLATS SOIL

TEST	LEACH DAY NO.	REPS (N)	LEACH DAY NO.	PH	TOC [.1](a)	OXALATE [.12]	CL- [.03]	CA [.01]	K [.3]	ZN [.02]	AL [.03]	MG [.06]	CO [.01]	FE [.005]	MN [.002]	NI [.02]	SR [.002]	BALANCE DIF/SUM
CONTROL	1	2	AVERAGE	5.19	27.4		0.4	3.0	2.0	0.03	0.55	0.6		0.141	1.575		0.015	-0.126
CONTROL	2	1		5.21	26.3		0.5	2.8	1.3	0.02	0.53	0.6		0.156	1.550		0.014	-0.123
CONTROL	5	2	AVERAGE	5.25	29.2		0.5	2.5	1.7	0.02	0.53	0.5		0.147	1.470		0.012	-0.072
CONTROL	9	1		5.23	29.3		0.5	2.4	1.4		0.53	0.5		0.135	1.270		0.012	-0.405
CONTROL	15	1		5.25	25.1		0.1	2.5	1.5	0.01	0.52	0.5		0.093	0.397		0.012	0.136
CONTROL	1 TO 15	7	AVERAGE	5.22	27.8		0.4	2.7	1.7	0.02	0.54	0.5		0.139	1.372		0.013	-0.113
CONTROL	1 TO 15	7	STD DEV	(±0.06)	(±1.6)		(±0.1)	(±0.3)	(±0.4)	(±0.01)	(±0.03)	(±0.1)		(±0.021)	(±0.382)		(±0.001)	(±0.207)
EXPOSED:																		
HC16	1	2	AVERAGE	4.14	39.0	2.9	107.4	21.5	4.0	38.00	2.84	3.1	0.03	0.112	11.350	0.04	0.113	-0.007
HC17	1	5	AVERAGE	4.16	34.1	2.5	106.4	19.8	3.6	44.86	2.15	2.9	0.03	0.084	10.030	0.04	0.102	-0.039
HC17	1	5	STDEV	(±0.03)	(±0.9)	(±0.2)	(±2.3)	(±0.3)	(±0.1)	(±1.87)	(±0.07)	(±0.1)	(±0.00)	(±0.003)	(±0.333)	(±0.00)	(±0.001)	(±0.026)
HC18	1	2	AVERAGE	4.03	37.9	3.6	136.0	21.9	3.9	57.85	3.27	3.1	0.03	0.108	11.050	0.05	0.113	-0.021
HC19	1	2	AVERAGE	4.15	37.2	2.7	115.8	20.6	3.8	50.10	2.36	3.0	0.03	0.086	10.500	0.04	0.107	-0.016
HC16-19	1	11	AVERAGE	4.13	36.2	2.8	113.6	20.6	3.8	46.93	2.52	3.0	0.03	0.094	10.541	0.04	0.107	-0.021
HC16-19	1	11	STD DEV	(±0.06)	(±2.2)	(±0.4)	#####	(±1.0)	(±0.2)	(±6.78)	(±0.46)	(±0.1)	(±0.00)	(±0.013)	(±0.632)	(±0.00)	(±0.005)	(±0.014)
HC17	2	1		4.26	28.5	1.5	108.7	20.1	3.6	42.70	1.83	2.9	0.03	0.099	11.200	0.04	0.106	0.002
HC16	5	2	AVERAGE	4.21	28.5	0.1	103.9	21.7	4.2	36.00	1.44	3.1	0.05	0.090	14.750	0.05	0.116	-0.037
HC17	5	5	AVERAGE	4.34	26.0	0.1	111.9	20.0	4.2	41.76	1.10	2.9	0.04	0.077	13.140	0.04	0.105	-0.039
HC17	5	5	STDEV	(±0.01)	(±0.4)	(±0.0)	(±2.7)	(±0.4)	(±0.1)	(±1.89)	(±0.05)	(±0.0)	(±0.00)	(±0.009)	(±0.336)	(±0.00)	(±0.001)	(±0.026)
HC18	5	2	AVERAGE	4.19	29.8	0.1	131.3	22.7	4.3	57.20	1.79	3.2	0.06	0.092	15.750	0.05	0.122	-0.015
HC19	5	2	AVERAGE	4.28	29.1		120.3	20.8	2.3	47.60	1.12	3.0	0.04	0.064	13.600	0.03	0.112	-0.044
HC16-19	5	11	AVERAGE	4.28	27.7	0.1	116.6	20.9	3.9	44.58	1.29	3.0	0.05	0.080	13.991	0.04	0.111	-0.034
HC16-19	5	11	STD DEV	(±0.07)	(±1.8)	(±0.0)	(±9.2)	(±1.1)	(±0.8)	(±7.34)	(±0.28)	(±0.1)	(±0.01)	(±0.012)	(±1.090)	(±0.01)	(±0.007)	(±0.013)
HC17	9	1		4.38	25.3	0.1	111.6	19.8	3.8	40.90	0.98	3.0	0.05	0.083	14.400	0.04	0.106	-0.056
HC17	15	1		4.39	24.0		114.6	20.1	2.8	40.30	0.82	3.0	0.06	0.063	16.100	0.03	0.109	-0.013
HC16-19	OVERALL	25	AVERAGE	4.22	31.2	1.7	114.7	20.7	3.8	45.22	1.82	3.0	0.04	0.086	12.462	0.04	0.109	-0.026
HC16-19	OVERALL	25	STD DEV	(±0.10)	(±5.0)	(±1.4)	(±9.8)	(±1.0)	(±0.6)	(±6.72)	(±0.74)	(±0.1)	(±0.01)	(±0.014)	(±2.049)	(±0.00)	(±0.006)	(±0.018)
HC22A	1	2	AVERAGE	4.86	29.6	not determ	10.0	5.2	2.90	0.59	0.6	1.0	<	0.1	2.945	<	0.026	-0.024
HC22A	5	2	AVERAGE	5.05	29.3	not determ	9.0	4.7	1.50	0.51	0.5	0.9	<	0.1	3.105	<	0.023	0.054
HC22B	1	2	AVERAGE	4.16	41.6	3.4	90.5	19.0	3.30	30.15	2.2	2.9	0.0	0.1	10.770	0.03	0.101	-0.003
HC22B	5	2	AVERAGE	4.41	29.7	not determ	88.4	18.6	2.80	28.40	1.0	2.9	0.0	0.1	12.950	<	0.100	-0.023
ACIDIFIED (+HCL)	CONTROL 5	1		4.49	24.3		42.2	12.5	4.0	0.08	0.62	2.2	0.02	0.070	7.840		0.065	-0.153
	10	1		4.43	19.2		44.8	14.1	4.8	0.10	0.64	2.4	0.01	0.058	7.080	0.01	0.073	0.129

(a) estimated detection limits, µg/mL; table values are in terms of µg/mL in the extraction solution (1:10 soil:solution ratio)

Over the 15-day study, most species listed increased slightly in the Burbank controls and exposed soils (Table 3.17), except for the slight decrease in soluble Zn from the exposed soils with time. For Maxey Flats controls and exposed aliquots, the trend was generally toward steady to slightly decreasing concentrations with time. Delaying water contact for two days following exposure had no significant effect on the extracts of either soil, so that data is averaged into the HC-17 results. In Burbank controls, essentially all the soluble P is as phosphate; in Maxey Flats, P and phosphate are both at or below detection limits (0.1 mg P/L in solution). Nitrate is not included in the Maxey Flats data (Table 3.18), because levels in both control and exposed-soil extracts are high (13-17 mg/L) and comparable.

Evaporation would generally account for increase in Cl^-, Ca, K, Sr content for Burbank, if also corrected for control concentrations. For Maxey Flats controls and exposed aliquots (Table 3.18), the trend was generally toward steady to slightly decreasing concentrations with time, suggesting slight mineralization losses. Ritzville, Quillayute, Shawano, and Yamac exposed soils generally show Cl^- increases that reflect the evaporation rate (Table 3.19). Using the Cl/Zn ratios determined for aerosol mass filters (see Table 3.6), the total Zn deposited can be estimated. Soluble Zn at 1 day reflects the following percent of those estimated totals: Burbank, 12.5%; Maxey Flats, 32.6%; Ritzville, 6.7%; Quillayute, 19.4%; Shawano, 5.0%; Yamac, 0.1%. Soluble Zn and Al generally declines further with time in all exposed soils, supporting a mineralization hypothesis (Figure 3.19). DOC levels generally decrease with time in both control and exposed soils, but exposed Quillayute shows initial marked increase over control (Figure 3.20). Delaying water contact for two days following exposure had no significant effect on the extracts of any of the tested soils, so that data is averaged into the HC17 results.

In Burbank controls, essentially all the total soluble P (not itemized in tables) was as phosphate; in Maxey Flats, P and phosphate were both at or below detection limits (0.1 mg P/L in solution). Ritzville P levels were low, and less than half appeared to be as PO_4^{3-}. Shawano and Yamac showed essentially nondetectable PO_4^{3-} levels; total P for controls/acidified/exposed at 5-day extraction were 1.33/1.12/0.99 and 0.079/0.050/0.023 g/mL for Shawano and Yamac, respectively. Though the concentrations are low, the suggestion of increased mineralization of P is apparent.

Cumulative Dose Exposures. Soil lenses were not subjected to multiple exposures during the cumulative dose tests, because the thin lens technique already maximizes aerosol to soil concentrations. Duplicate aliquots of Burbank and Maxey Flats soils were exposed during tests HC-22A and HC-22B (55% RH, 2 mph, 3-h duration) in same manner as earlier exposures. Subsamples were removed after 1 and 5 days of water contact, and analyzed as above. An incubator malfunction caused the temperature to rise to 31°C for the first day,

TABLE 3.19. COMPARISON OF SOLUBLE SPECIES IN HC EXPOSED SOILS TO CONTROL SOILS - RITZVILLE, QUILLAYUTE, SHAWANO, AND YAMAC SOILS

DOSE TYPE	LEACH DAY	REPS (N)	PH	DOC [.1](a)	CL- [.03]	NO3- [.06]	PO4- [.1]	SO4= [.1]	CA [.01]	NA [.01]	ZN [.02]	AL [.03]	MG [.06]	BA [.002]	K [.3]	LI [.004]	FE [.005]	MN [.002]	SI [.02]	SR [.002]	BALANCE DIFF/SUM
Ritzville Soil																					
CONTROL	1	2	7.40	3.9	0.1	1.7	0.7	0.6	1.7	0.52	<	0.08	0.6	0.006	2.6	<	0.128	0.006	8.8	0.007	0.004
CONTROL	2	1	7.45	3.7	0.2	2.1	0.8	0.6	1.7	0.47	<	0.12	0.7	0.005	2.5	<	0.160	0.003	11.0	0.008	0.010
CONTROL	5	2	7.48	3.7	0.2	1.8	1.2	0.6	1.8	0.61	<	0.14	0.7	0.006	2.9	0.004	0.196	0.002	14.5	0.008	-0.018
CONTROL	9	1	7.45	3.5	0.2	2.3	1.2	0.7	2.1	0.62	<	0.16	0.8	<	2.5	0.005	0.248	0.002	16.8	0.009	-0.096
CONTROL	15	1	7.57	3.0	0.2	3.3	1.4	1.0	2.3	0.77	<	0.23	0.9	0.007	2.4	0.012	0.344	0.002	18.8	0.010	0.118
HC17-EXP	1	3	5.96	7.2	104.1	1.7	0.1	1.6	31.2	0.93	8.43	<	12.1	0.160	9.0	0.028	<	0.353	10.4	0.151	0.014
(±STD DEV)			(±0.20)	(±0.30)	(±1.25)	(±0.07)	(±0.02)	(±0.16)	(±0.61)	(±0.03)	(±0.68)		(±0.26)	(±0.001)	(±0.4)	(±0.00)		(±0.35)	(±0.41)	(±0.003)	(±0.009)
HC17-EXP	2	1	6.14	6.4	104.8	1.8	0.1	1.7	31.6	1.07	7.15	<	12.3	0.150	9.3	0.029	0.008	0.372	13.6	0.154	0.016
HC17-EXP	5	3	6.24	4.9	108.0	1.8	0.1	1.5	31.8	1.10	7.50	<	12.4	0.162	9.6	0.043	0.009	0.453	18.7	0.155	-0.014
(±STD DEV)			(±0.08)	(±0.50)	(±0.97)	(±0.03)	(±0.07)	(±0.16)	(±0.32)	(±0.04)	(±0.35)		(±0.10)	(±0.007)	(±0.1)	(±0.01)		(±0.02)	(±0.40)	(±0.001)	(±0.028)
HC17-EXP	9	1	6.20	4.7	108.7	1.9	0.1	1.7	32.5	1.19	7.20	<	13.0	0.167	9.6	0.039	<	0.486	21.4	0.162	0.012
HC17-EXP	15	1	6.17	4.4	111.9	1.8	0.2	1.9	33.8	1.17	6.74	<	13.4	0.171	8.6	0.049	<	0.539	23.6	0.170	0.012
Quillayute Soil																					
CONTROL	1	2	5.32	134.6	2.4	0.1	<	2.8	4.2	2.23	0.01	1.56	1.8	0.058	2.5	0.004	0.113	0.641	1.6	0.034	0.228
CONTROL	2	1	5.87	112.7	2.6	<	<	3.3	2.5	2.06	<	1.00	1.2	0.027	2.1	<	0.123	0.663	1.9	0.019	0.512
CONTROL	5	2	5.81	99.8	2.8	<	<	3.8	2.1	1.99	<	0.84	0.9	0.024	1.8	<	0.260	0.892	2.0	0.016	0.464
CONTROL	9	1	6.01	102.0	2.9	<	<	3.4	1.5	1.81	<	0.78	0.6	0.017	1.1	<	0.289	0.829	1.8	0.011	0.331
CONTROL	15	1	5.91	81.1	3.5	<	<	3.0	1.2	1.88	<	0.88	0.5	0.015	1.2	0.002	0.502	0.741	1.9	0.009	0.470
HC17-EXP	1	3	4.45	148.9	111.8	0.7	<	1.1	26.8	2.92	25.70	3.21	6.8	0.636	5.5	0.018	0.083	4.030	1.7	0.241	0.028
(±STD DEV)			(±0.03)	(±3.80)	(±3.35)	(±0.28)		(±0.14)	(±1.22)	(±0.10)	(±2.26)	(±0.26)	(±0.29)	(±0.036)	(±0.2)	(±0.01)	(±0.01)	(±0.19)	(±0.05)	(±0.012)	(±0.016)
HC17-EXP	2	1	4.65	155.1	116.4	0.6	<	1.2	27.7	2.91	22.90	2.91	7.1	0.622	5.6	0.021	0.096	4.790	2.2	0.251	0.034
HC17-EXP	5	3	4.63	90.5	116.5	.2,<	<	0.8	27.5	3.05	16.33	1.11	7.3	0.565	5.8	0.026	0.078	7.127	2.4	0.247	-0.015
(±STD DEV)			(±0.04)	(±5.80)	(±2.35)			(±0.06)	(±0.09)	(±0.05)	(±0.95)	(±0.14)	(±0.14)	(±0.029)	(±0.4)	(±0.00)	(±0.01)	(±0.44)	(±0.20)	(±0.001)	(±0.029)
HC17-EXP	9	1	4.68	81.1	121.7	<	<	0.9	26.9	3.25	13.90	0.82	7.5	0.561	5.5	0.024	0.155	10.800	2.6	0.247	-0.043
HC17-EXP	15	1	4.74	72.7	124.6	<	<	1.1	25.7	3.36	13.90	0.56	7.5	0.542	4.6	0.020	0.141	15.200	2.6	0.238	0.015
Shawano Soil																					
CONTROL	1	2	5.70	144.6	1.0	0.3	2.7	5.5	12.4	0.48	0.13	1.34	3.2	0.159	3.5	0.013	0.267	4.295	1.2	0.078	0.284
CONTROL	2	1	6.30	117.5	1.1	<	1.8	5.6	9.1	0.39	0.08	0.83	2.2	0.081	3.3	<	0.214	3.710	1.5	0.056	0.622
CONTROL	5	2	6.77	123.3	0.5	<	1.9	6.4	6.8	0.40	0.06	0.66	1.4	0.071	3.6	0.006	0.460	3.625	1.9	0.041	0.539
CONTROL	9	1	6.97	132.9	0.1	<	1.6	7.9	6.9	0.35	0.03	0.66	1.4	0.077	3.3	<	0.931	4.360	2.5	0.041	0.309
CONTROL	15	1	7.09	133.2	1.2	<	1.6	8.4	6.7	0.37	0.06	0.77	1.3	0.079	3.4	0.008	1.440	4.610	2.5	0.039	0.564
HC17-EXP	1	3	4.92	215.6	107.9	4.8	4.3	7.8	48.6	0.87	6.47	2.05	11.4	0.470	7.6	0.032	0.353	15.367	1.5	0.316	0.150
(±STD DEV)			(±0.07)	(±14.4)	(±4.22)	(±0.07)	(±0.53)	(±1.02)	(±1.88)	(±0.03)	(±0.26)	(±0.12)	(±0.44)	(±0.023)	(±0.3)	(±0.00)	(±0.03)	(±0.45)	(±0.04)	(±0.005)	(±0.015)
HC17-EXP	2	1	5.58	179.3	110.0	<	1.3	8.3	43.6	0.80	4.70	1.43	10.4	0.428	7.4	0.031	0.213	15.800	1.9	0.292	0.139
HC17-EXP	5	3	5.76	136.4	111.0	<	0.8	8.9	36.6	0.78	2.91	0.56	8.9	0.402	7.8	0.031	0.213	18.233	2.7	0.246	0.058
(±STD DEV)			(±0.14)	(±3.0)	(±2.49)		(±0.09)	(±0.19)	(±0.91)	(±0.07)	(±0.17)	(±0.05)	(±0.27)	(±0.008)	(±0.1)	(±0.01)	(±0.01)	(±0.95)	(±0.05)	(±0.007)	(±0.042)
HC17-EXP	9	1	6.14	139.8	114.3	<	0.5	10.1	33.0	0.80	2.19	0.45	8.4	0.413	8.0	0.036	0.308	20.200	3.7	0.228	-0.004
HC17-EXP	15	1	6.36	151.0	116.4	<	0.8	2.7	27.8	0.78	1.55	0.38	7.1	0.364	7.4	0.026	0.367	18.200	4.4	0.194	0.122
Yamac Soil																					
CONTROL	1	2	9.42	23.6	27.4	1.1	2.2	16.4	3.6	96.40		1.26	0.8	0.013		0.012	0.643	0.008	6.5	0.014	0.027
CONTROL	2	1	9.11	21.2	27.8	1.2	2.2	17.7	4.1	108.00	0.03	1.39	1.0	0.012	<	0.004	0.721	0.007	7.5	0.015	0.024
CONTROL	5	2	8.85	20.6	25.5	1.8	2.2	19.6	4.1	128.50	<	0.44	1.0	0.008	0.1	0.011	0.246	0.002	6.0	0.019	0.019
CONTROL	9	1	8.82	17.6	29.1	3.4	2.2	20.9	4.9	137.00	<	0.66	1.2	0.012	<	0.007	0.391	0.004	6.8	0.020	0.002
CONTROL	15	1	8.86	17.2	29.6	9.0	2.0	20.5	4.7	146.00	<	0.35	1.3	0.007	<	0.014	0.234	0.001	6.4	0.019	0.024
HC17-EXP	1	3	8.72	26.5	141.9	1.2	0.5	17.5	6.6	142.33	0.12	0.20	1.7	0.011	0.1	0.012	0.127	0.008	3.7	0.038	0.008
(±STD DEV)			(±0.09)	(±1.46)	(±2.40)	(±0.16)	(±0.06)	(±0.30)	(±0.29)	(±5.10)	(±0.03)	(±0.06)	(±0.08)	(±0.001)		(±0.01)	(±0.03)	(±0.01)	(±0.29)	(±0.001)	(±0.013)
HC17-EXP	2	1	8.56	20.4	143.7	0.6	0.4	18.6	7.3	151.00	0.10	0.13	2.0	0.011	<	0.021	0.091	0.006	4.1	0.045	-0.003
HC17-EXP	5	3	8.60	19.1	147.4	1.0	0.5	20.7	8.4	153.33	0.12	0.07	2.4	0.012	0.5	0.024	0.058	0.018	4.4	0.051	0.001
(±STD DEV)			(±0.01)	(±0.50)	(±2.50)	(±0.43)	(±0.04)	(±0.20)	(±0.17)	(±4.60)	(±0.00)	(±0.02)	(±0.05)	(±0.001)		(±0.00)	(±0.00)	(±0.00)	(±0.05)	(±0.001)	(±0.009)
HC17-EXP	9	1	8.61	17.8	148.6	0.8	0.6	22.0	8.9	169.00	0.11	0.05	2.7	0.015	<	0.024	0.041	0.021	4.5	0.055	0.001
HC17-EXP	15	1	8.64	17.8	152.7	[illegible]	[illegible]	20.9	9.2	168.00	0.11	0.08	2.7	0.011	<	0.024	0.078	0.019	4.6	0.054	0.000

(a) estimated detection limits, µg/mL; table values [illegible] of µg/mL in the extraction solution (1:10 soil:solution ratio)

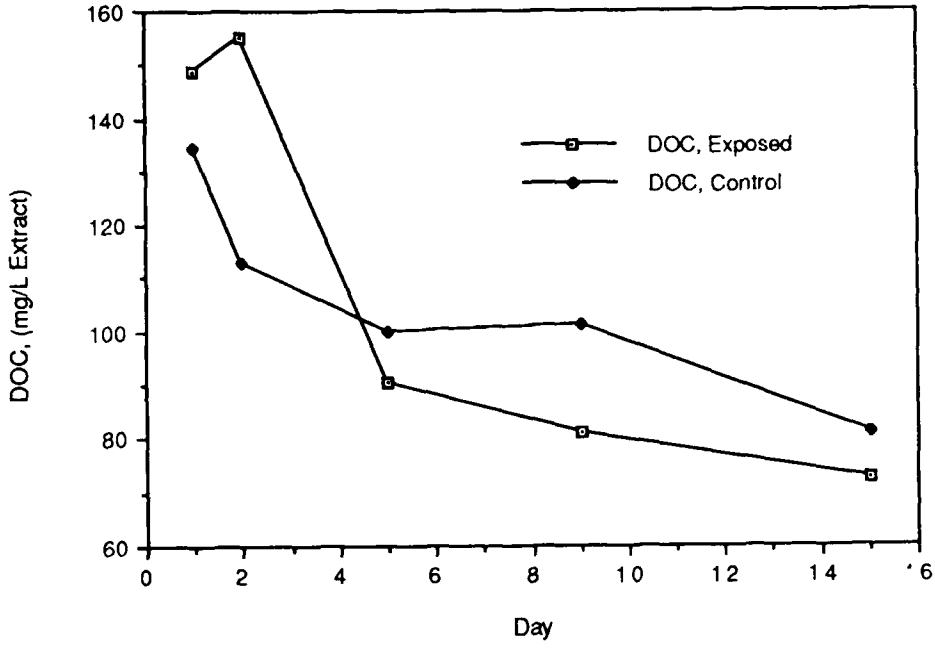


FIGURE 3.20. DOC LEVELS WITH TIME, FOR HC-EXPOSED VS. CONTROL QUILLAYUTE LEACHATES

followed by slightly erratic temperature control (23-25°C) for the remaining 4 days. Although the target concentrations were 120 and 600 mg/m^3 for the A and B series, respectively, since the exposure duration was reduced from 4 to 3 h per day, the effective expected Zn deposition to soils during HC-22B should be very similar to that found during the HC-16 through HC-19 relative humidity test series.

Comparisons of selected soluble components for Burbank and Maxey Flats are included in Tables 3.17 and 3.18, respectively. Based on Cl^- determinations, deposition to the B series soils was roughly 80% of the average deposition during HC-16 through HC-19. Generally, the A and B series intrinsic soil component dissolution concentrations tended to bracket the values from the acidified control, supporting the hypothesis that most effects could be attributed to the acidity shift. Exceptions were noted for DOC, NO_3^-, and PO_4^{-3} in Maxey Flats, but all these parameters may be tied to the effects of smoke deposition on the microbial activity. Solubility of Zn in the Burbank system was significantly lower in the B test than in the earlier tests; in Maxey Flats extracts, Zn solubility was somewhat depressed, compared to total Cl^- levels. While Maxey Flats replicates showed deviation in pH of no more than 0.03 units, Burbank showed a greater range, particularly at day 1: a difference of 0.16 pH units for

0.00 and 0.14 pH units, respectively. Only SO_4^{2-} seemed significantly altered in the replicates, showing a range of 1.66 to 2.16 g/mL at day 1, B series; by day 5, SO_4^{2-} concentration had dropped to 1.5 μg/mL. The higher initial incubation temperature may have contributed to the effects seen in the poorly buffered Burbank system.

Comparison of Exposed to Acidified Control Soils. Based on observed responses, control soils were stressed with an appropriate acid (HCl) concentration, to determine whether changes in soluble species distribution could be attributed to simple pH effect (Table 3.20). The amount of HCl estimated to be required to approximate the change in pH on exposed soils (0.1 mmol acid/10 g soil) was added to the HC16 controls following their initial 5-day equilibration, and the solutions sampled at 5 and 10 days following acidification. With time of extraction, the pH increased in these acidified contacts to levels fairly representative of the levels seen in the exposed soils (Table 3.21). The observed soluble species in exposed soils were paralleled somewhat by the acidification of control soil for most analytes. Several species (Ca, Mg, Ba, K, Li, Sr) showed lower soluble concentrations in acidified than in exposed soils, but consistently midrange between exposed and control soils, suggesting that increased acid addition could result in similar concentrations of solubles. Levels of soluble Mn in exposed soils were less consistently reflected in acidified controls, particularly in Burbank and Ritzville; however, higher soluble Mn levels did seem to reflect simple acidity levels much like the Ca group. Fe levels in acidified controls increased in Quillayute and Shawano only, relative to controls; all soils showed decreased soluble Fe with HC exposure. Si levels fluctuated with acidification and exposure, but in all cases were within 25% of each other, and so are considered reasonably well reproduced. Soluble NO_3^- and PO_4^{3-} in acidified soils paralleled levels in controls for Burbank. For Maxey Flats, nitrate levels were elevated in all fractions. Yamac showed marked increase in NO_3^- when acidified, reaching 11 mg/mL in solution at 10 days, compared to exposed soil NO_3^- levels of 0.9 mg/mL at 10 days; PO_4^{3-} fell below detection limits. Ritzville also shows depression of NO_3^- in HC exposed soils, while Quillayute and Shawano show limited detectable NO_3^- under all conditions. For PO_4^{3-}, exposed soils showed levels at detection limit for Ritzville, while Quillayute values were all below detection. Shawano exposed soils showed rapid decrease in soluble PO_4^{3-}. Most likely explanation is the interruption of normal microbial activity in the case of NO_3^-, and precipitation of PO_4^{3-} upon addition of Al.

TABLE 3.20. COMPARISON OF SOLUBLE SPECIES RESULTING FROM ACIDIFICATION EXPOSURE, AND COMPARED TO CONTROL SOILS

SOIL	DOSE TYPE	LEACH DAY	REPS (N)	PH	TOC [.1](a)	CL- [.03]	NO3- [.05]	PO4- [.1]	SO4= [.1]	CA [.01]	NA [.01]	ZN [.02]	AL [.03]	MG [.06]	BA [.002]	K [.3]	LI [.004]	FE [.005]	MN [.002]	SI [.02]	SR [.002]	BALANCE DIFF/SUM
RITZVILLE	CONTROL	5	2	7.48	3.7	0.2	1.7	1.2	0.6	1.8	0.61		0.14	0.69	0.006	2.9	0.004	0.196	0.002	14.50	0.008	-0.047
RITZVILLE	CONTR+ H+	5	1	6.18	2.2	44.2	3.6	0.8	0.7	12.8	1.07		0.04	4.96	0.057	7.0	0.025	0.039	0.013	22.40	0.062	-0.040
RITZVILLE	EXPOSED	5	3	6.24	4.9	108.0	1.8	≤.14	1.5	31.8	1.10	7.50		12.40	0.162	9.6	0.043	0.009	0.453	18.73	0.155	-0.014
QUILLAYUTE	CONTROL	5	2	5.81	99.8	2.4			3.8	2.1	1.99		0.84	0.92	0.024	1.8		0.260	0.892	1.95	0.016	0.464
QUILLAYUTE	CONTR+ H+	5	1	5.20	82.5	47.3			1.6	7.5	2.64		0.48	3.25	0.126	4.6	0.016	0.343	5.340	2.09	0.065	-0.098
QUILLAYUTE	EXPOSED	5	3	4.63	90.5	116.5	≤.2		0.8	27.5	3.05	16.33	1.11	7.28	0.565	5.8	0.026	0.078	7.127	2.41	0.247	-0.015
SHAWANO	CONTROL	5	2	6.77	123.3	1.0		1.9	6.4	6.8	0.40	0.06	0.66	1.44	0.071	3.6	0.006	0.460	3.625	1.92	0.041	0.540
SHAWANO	CONTR+ H+	5	1	6.45	124.6	45.9		1.3	8.2	11.2	0.54	0.06	0.58	2.74	0.136	5.9	0.020	0.624	6.320	2.27	0.073	-0.084
SHAWANO	EXPOSED	5	3	5.76	136.4	111.0		0.8	9.1	36.6	0.78	2.91	0.56	8.92	0.402	7.8	0.031	0.213	18.233	2.74	0.246	0.058
YAMAC	CONTROL	5	2	8.85	20.6	27.4	1.2	2.1	19.6	4.1	129		0.44	1.00	0.008	0.1	0.011	0.246	0.002	8.03	0.019	0.018
YAMAC	CONTR+ H+	5	1	8.81	15.3	72.5	4.4	1.5	21.3	6.3	156		0.14	1.72	0.008	0.2	0.014	0.119	0.011	5.36	0.028	-0.014
YAMAC	EXPOSED	5	3	8.60	19.1	150.8	1.1	0.5	20.7	8.4	163	0.12	0.07	2.41	0.012	0.5	0.024	0.058	0.018	4.41	0.051	0.001
BURBANK	CONTROL	5	2	7.87	5.3	0.1	2.7	1.9	0.8	5.9	0.30	0.03	0.04	1.20	0.005	11.8	0.005	0.036	0.004	6.55	0.023	0.020
BURBANK	CONTR+ H+	5	1	6.66	4.8	44.0	4.0	2.0	1.0	14.5	0.41			3.04	0.027	16.5	0.020	0.020		10.00	0.061	-0.028
BURBANK	EXPOSED	5	5	6.24	6.1	103.5	0.8	0.2	1.8	32.0	0.50	12.30		6.70	0.085	20.5	0.029	0.009	0.251	8.19	0.144	0.007
MAXEY FLAT	CONTROL	5	2	5.25	29.2	0.4	14.4		5.5	2.5	0.20	0.02	0.53	0.50	0.029	1.7	0.008	0.147	1.470	1.16	0.012	-0.044
MAXEY FLAT	CONTR+ H+	5	1	4.49	24.3	44.4	16.9		5.3	12.5	0.37	0.08	0.62	2.20	0.214	4.0	0.014	0.070	7.840	1.63	0.065	-0.151
MAXEY FLAT	EXPOSED	5	5	4.34	26.0	111.9	16.2		5.1	20.0	0.36	41.76	1.10	2.80	0.437	4.2	0.018	0.077	13.140	1.53	0.105	-0.039

(a) estimated detection limits, µg/mL; table values are in terms of µg/mL in the extraction solution (1:10 soil:solution ratio)

TABLE 3.21. PH VALUES REFLECTED BY CONTROL, ACIDIFIED CONTROL, AND HC AEROSOL-EXPOSED SOILS

Soil	Control		Acidified		Exposed	
	Day 1	Day 5	Day 0	Day 5	Day 1	Day 5
	(pH units)					
Burbank	7.85	7.84	5.03	6.66	6.29	6.38
Maxey Flats	5.10	5.25	3.21	4.49	4.12	4.27
Yamac	9.33	8.85	7.73	8.81	8.72	8.60
Ritzville	7.40	7.47	4.45	6.18	5.84	6.24
Shawano	5.6	6.8	5.35	6.45	4.92	5.76
Quillayute	5.24	5.80	4.06	5.20	4.45	4.63
N	2	2	1	1	3,9[a]	3,9[a]
Wet deposition plates, HC-17 [b]: 3.56						

(a) 9 samples over %RH range for Burbank and Maxey Flats; 3 samples at midrange % RH for other soils.
(b) Typical wet deposition plate used to estimate amount of acid needed to add to the acidified control.

3.4 CHLOROCARBON MASS LOADING ON AND DEPOSITION VELOCITIES TO FOLIAR SURFACES AND SOILS

A variety of physical and environmental factors combine to determine the rate at which atmospheric pollutants transfer from the air column, through the near-surface boundary layer, to a receptor surface. These factors, which include various atmospheric conditions such as wind speed and humidity, aerosol diameter, contaminant vapor pressure particularly in the case of organic residues, and the physical and chemical structure of the receptor surface, combine to determine the net deposition to a surface.

Two different removal mechanisms operate on atmospheric pollutants, one for gas-phase compounds and one for compounds found in the aerosol phase. Although these two deposition mechanisms are governed by different parameters, the net deposition to a surface can be calculated when an overall gas/aerosol deposition velocity is known. A deposition velocity, which is normally expressed as V_d in units of cm/s, is analogous to a mass transfer coefficient and describes the rate at which an atmospheric pollutant is deposited on a given surface. Without the deposition velocity, the dosing levels to a receptor surface cannot be predicted.

To quantify the relationship between chemical dosage and damage or effect, the gas and aerosol concentration, deposition velocity, and surface exposure time must all be known to estimate the total surface deposition, or mass loading (ML). Because of the complexity of deposition processes, specific deposition velocities are rarely known, and therefore must be either measured directly or calculated. In this study we have directly measured surface ML by subsampling a known area of an exposed surface, and then extracting and quantifying any deposited chemical species. Subsequently, these data were combined with the measured gas/aerosol concentrations and exposure times to compute the deposition velocity. The formula for calculating V_d is presented in Equation (3). Quantifying the

$$V_d\ (cm/s) = \frac{ML(ng\ compound/cm^2\ leaf)}{aerosol\ conc\ (ng\ compound/m^3)} \times \frac{1 \times 10^6\ cm^3}{m^3} \times \frac{1}{exposure\ time} \qquad (3)$$

deposition process for specific receptor surfaces permits a comparison of the relative importance of atmospheric variables and canopy and receptor surface (plant and soil) characteristics to the net deposition efficiency.

3.4.1 Chlorocarbon Deposition to Vegetative Surfaces

The methodology used for plant exposure and analysis has been discussed in Section 2.0. Five species of plants were exposed during each test of the relative humidity experiments. Four different relative humidity (RH) experiments were conducted: HC-16 (RH=20%), HC-17 (RH=55%), HC-18 (RH=90%), and HC-19 (first half, RH=55%; second half, RH=95%). These humidities were selected to cover the range of relative humidities expected in the natural environment. The concentrations of chlorinated hydrocarbons released from the HC smoke generation were monitored in the wind tunnel experimental test section and found to be relatively consistent between tests.

The mass loadings obtained from the chemical analysis of the exposed plant tissues are given in Table 3.22. In most cases, the mass loadings of the chlorinated hydrocarbons on the plant foliage were very low and fell in the range of 1 to 10 ng/cm^2. The notable exception to this observation concerns the surface concentrations of C_6Cl_6 on sagebrush. In this case the mass loading is an order of magnitude greater (120-170 ng/cm^2), although compared to the measured air concentrations this is still fairly low. This observation may be related to the rough, relatively high surface area, and relatively complex waxy cuticular surface of the sagebrush foliage. The resistance to aerosol deposition would be decreased by the nature of the surface. It was also observed that the mass loading for C_6Cl_6 is greater

than for the other three compounds on all five plant species. This is reasonable as C_6Cl_6 is primarily transported adsorbed to particulates, and in general, particulates have less resistance to deposition than do gases.

It is likely that some of the more volatile compounds (CCl_4, C_2Cl_4, and C_2Cl_6) that were deposited to the plant foliage rapidly evaporated, in which case the net ML to the plant surface would be the sum of aerosol deposition to and gas adsorption by the plant surfaces, minus any evaporative losses from surfaces. The parameters that influence the mechanism of gas adsorption to a surface are highly dependent on the physical/chemical properties of the gas. These properties will influence the interactions a gas has with the adsorption sites on the surface. A gas can also dissolve into the leaf cuticle, partitioning between the gaseous and dissolved states on the basis of Henry's Law constant. Chemically, both these mechanisms for gas exchange are more complex than aerosol deposition. The aerosol deposition mechanism is highly dependent on the aerodynamic mass median diameter of the aerosol, the roughness of the receptor surface, and is relatively independent of the chemical composition of an aerosol.

3.4.2 Chlorocarbon Deposition to Soil Surfaces

The soil deposition results for three of the RH exposure tests are presented in Table 3.23. The concentrations of the chlorinated hydrocarbons in aerosol contaminated soils were generally an order of magnitude greater than that found on plant foliage, and ranged from 30 to 100 ng/cm^2 for CCl_4, C_2Cl_4 and C_6Cl_6 to <10 ng/cm^2 for C_2Cl_6. This implies that gaseous adsorption was playing an important role in transferring the material to the soil surface, with substantially less revolatilization than was noted for foliar surfaces. Thus, the soil surfaces appear to provide a greater opportunity for gas adsorption than the plant surfaces. Soils are know to adsorb organic compounds onto both their organic and inorganic surfaces, and its likely that an active adsorption mechanism is responsible for this observation. This adsorption mechanism may explain not finding C_2Cl_6 in extractable quantities in the soil deposition samples. Further evidence in support of the active soil adsorption theory is that residence times of the deposited materials were generally much longer on soils than plants (see Section 3.5).

The Burbank soil showed ML that were statistically very similar to those measured on the Maxey Flats soil ($P>0.1$). This implies that the number or type of adsorption sites found on the two soils is very similar for the dose level employed. It is not clear if the adsorption is taking place on organic matter, or at inorganic exchange sites; a more in-depth study would be necessary to precisely define the mechanism of chlorocarbon adsorption onto these soils.

TABLE 3.22. NET MASS LOADING OF CHLOROCARBONS TO PLANT FOLIAGE EXPOSED TO HC SMOKE DURING THE RELATIVE HUMIDITY EXPERIMENTS[a]

Plant Species/ Experiment Code	Chemical Species			
	CCl_4	C_2Cl_4	C_2Cl_6	C_6Cl_6
Bush Bean				
HC16	2.6 (± 0.6)	2.8 (± 1)	1.3 (± 0.8)	1.1(± 6)
HC17	2.2 (± 2)	2.3 (± 1)	4.4 (± 1)	7.6 (± 3)
HC18	2.9 (± 0.9)	6.4 (± 6)	4.9 (± 2)	14 (± 6)
HC19	1.9 (± 0.9)	6.3 (± 1)	9.4 (± 1)	12 (± 2)
Average	2.4 (± 0.5)	4.4 (± 2)	5.0 (± 3)	11 (± 3)
Ponderosa Pine				
HC16	4.5 (± 0.8)	25 (± 10)	8.5 (± 6)	22 (± 20)
HC17	6.2 (± 2)	23 (± 8	18 (± 6)	22 (± 10)
HC18	1.6 (± 1)	15 (± 5)	9.2 (± 5)	38 (± 10)
HC19	1.9 (± 1)	12 (± 6)	9.4 (± 6)	19 (± 9)
Average	3.6 (± 2)	19 (± 6)	11 (± 4)	25 (± 9)
Sagebrush				
HC16	6.6 (± 2)	4.2 (± 3)	5.0 (± 2)	160 (± 60)
HC17	5.8 (± 2)	5.8 (± 3)	8.8 (± 6)	120 (± 80)
HC18	9.9 (± 2)	9.4 (± 3)	9.1 (± 6)	120 (± 70)
HC19	1.8 (± 0.6)	8.6 (± 2)	11 (± 1)	170 (± 70)
Average	6.0 (± 3)	7.0 (± 2)	8.5 (± 3)	150 (± 30)
Short-Needle Pine				
HC16	4.6 (± 3)	15 (± 9)	3.1 (± 2)	5.5 (± 4)
HC17	8.4 (± 1)	16 (± 3)	11 (± 3)	8.1 (± 3)
HC18	8.0 (± 3)	13 (± 6)	5.5 (± 3)	13 (± 6)
HC19	1.7 (± 0.5)	11 (± 1)	7.7 (± 0.7)	11 (± 4)
Average	5.7 (± 3)	14 (± 2)	6.9 (± 4)	9.4 (± 3)
Tall Fescue				
HC16	2.3 (± 1)	0.7 (± 0.3)	0.87 (± 1)	17 (± 10)
HC17	1.0 (± 0.3)	1.9 (± 0.4)	9.3 (± 0.9)	13 (± 10)
HC18	2.3 (± 0.6)	2.8 (± 1)	1.5 (± 1)	14 (± 10)
HC19	1.7 (± 1)	3.4 (± 2)	4.8 (± 3)	11 (± 7)
Average	1.8 (± 0.6)	2.2 (± 1)	2.0 (± 2)	14 (± 3)

(a) Mass loading values are given as average (± standard error of the mean) in ng/cm^2. Two samples were taken from five plants of each species, giving n =10. Detection limit was 0.1 ng/cm^2 leaf surface.

TABLE 3.23. MASS LOADING OF CHLOROCARBONS TO SOIL SURFACES EXPOSED TO HC SMOKE DURING THE RELATIVE HUMIDITY EXPERIMENTS [a]

Soil/ Experiment Code	Chemical Species			
	CCl_4 ML (±S.D.) ng/cm^2	C_2Cl_4 ML (±S.D.) ng/cm^2	C_2Cl_6 ML (±S.D.) ng/cm^2	C_6Cl_6 ML (±S.D.) ng/cm^2
Burbank Soil				
HC16	95 (± 6)	34 (± 9)	1.5 (± 3)	130 (± 30)
HC17	74 (± 20)	28 (± 10)	ND	64 (± 20)
HC18	37 (± 20)	100 (± 60)	ND	62 (± 30)
Average	68 (± 30)	55 (±40)	1.5	85 (± 40)
Maxey Flats Soil				
HC16	110 (± 30)	35 (± 10)	4.4 (± 5)	37 (± 7)
HC17	72 (± 20)	34 (± 6)	ND	18 (± 6)
HC18	120 (± 10)	83 (± 10)	9.4 (± 10)	12 (± 2)
Average	100 (± 30)	51 (± 30)	6.9 (± 4)	23 (± 10)

(a) Mass loading values are given as average (± standard error of the mean) in ng/cm^2. Two samples were taken from each of 3 soil coupons, giving n=6. Detection limit was1.0 ng/cm^2 soil surface.

3.4.3 Gas and Aerosol Phase Chlorinated Hydrocarbon Deposition Velocities to Plants and Soils Surfaces

The net deposition velocities that were computed using the ML values, exposure times, and measured air concentrations are given in Table 3.24. The relationship used for this calculation was given as Equation (3). The deposition velocities are termed "net" because the high vapor pressure of some of the chlorocarbons resulted in evaporation of an unknown portion of the aerosol after deposition on the receptor surface. It should also be noted that these values represent the average V_d from both aerosol and gas-phase deposition, as our experimental design does not allow differentiation of the two deposition mechanisms. As would be expected from the ML data, V_d values are a factor of 10 to 100 greater for soils than for foliar surfaces. In general, for foliage, V_d values for the four organic chlorinated species had the order $C_6Cl_6 > C_2Cl_6 = CCl_4 > C_2Cl_4$; for soils the order was $C_6Cl_6 = CCl_4 > C_2Cl_4 = C_2Cl_6$.

One reasonably clear observation can be made from these data concerning the relationship between the deposition velocities of the chlorinated organic compounds and the relative humidities: the highest V_d values were always found at the elevated humidities. In most cases, the differences between the maximum and minimum V_d values were statistically significant ($P > 0.2$). Elevated humidities affect the mechanisms for gas and aerosol

deposition in several ways. In the case of aerosol deposition, hygroscopic aerosol will tend to increase in diameter resulting in an increased V_d.

The deposition of gas phase compounds can also be effected by changes in humidity. It is possible for a change in relative humidity to cause a change in the adsorptive nature of the receptor surface. For some compounds, atmospheric water vapor can compete with a contaminant for the adsorption site. This does not appear to apply to the results obtained here, as the deposition of the gas phase compounds increases with increased concentrations of atmospheric water vapor. In this case it may be that the plant's stomata open in response to the increase water vapor, resulting an increase in the diffusions transport across the cuticular surface.

3.5 TERRESTRIAL PERSISTENCE

In the following section, the results of the HC relative humidity tests are discussed in terms of persistence of the chlorinated hydrocarbons on foliar and soil surfaces. Exponential regression lines were fit to the data sets and the slope of those lines were used to calculate the half-lives of the individual chemical species on the plant foliage and soil surfaces. These data are presented in Figures 3.21 through 3.27, and in Table 3.25. It is obvious that some of the data sets plotted have a notable amount of scatter, resulting in relatively poor fits by the exponential regression. This scatter is due in part to the variation of aerosol and gas deposition to structurally diverse plant canopies. Samples are collected and pooled from a variety of locations in the plant canopy to help minimize this variation. Some of the scatter may also be attributed to the analytical difficulties of extracting and quantifying the chlorocarbons in samples containing such trace amounts of material.

3.5.1 Persistence on Foliar Surfaces

Plant foliage was contaminated with aerosol and gas phase chlorocarbons generated during the HC relative humidity experiments. The foliar tissues were extracted and analyzed for CCl_4, C_2Cl_4, C_2Cl_6, and C_6Cl_6 for 4 days following exposure. The depuration of these compounds from the foliage of bush bean, ponderosa pine, sagebrush, short-needle pine and tall fescue are shown in Figures 3.21, 3.22, 3.23, 3.24, and 3.25, respectively.

TABLE 3.24. CHLOROCARBON NET DEPOSITION VELOCITIES (V_d) TO PLANT FOLIAGE AND SOIL SURFACES EXPOSED TO HC SMOKE DURING RELATIVE HUMIDITY EXPERIMENTS

Plant Species/ Experiment Code	Chemical Species			
	CCl_4	C_2Cl_4	C_2Cl_6	C_6Cl_6
	V_d (±S.D.) cm/s			
Bush Beans				
HC16	6.3 (± 2)E-05	1.9 (± 0.7)E-05	6.1 (± 4)E-05	4.2 (± 2)E-04
HC17	1.0 (± 0.8)E-04	2.7 (± 2)E-05	1.1 (± 0.3)E-04	3.6 (± 1)E-04
HC18	1.2 (± 0.4)E-04	6.4 (± 6)E-05	1.4 (± 0.7)E-04	9.4 (± 4)E-04
HC19	9.7 (± 5)E-05	9.9 (± 2)E-05	5.0 (± 0.7)E-04	4.8 (± 0)E-04
Average	9.6 (± 2) E-05	5.2 (± 4) E-05	2 .0(± 2)E-04	5.5 (± 3)E-04
Ponderosa Pine				
HC16	1.1 (± 0.2)E-04	1.7 (± 0.9)E-04	4.0 (± 3)E-04	8.3 (± 6)E-04
HC17	2.9 (± 0.7)E-04	2.7 (± 0.9)E-04	4.2 (± 1)E-04	1.1 (± 0.5)E-03
HC18	6.9 (± 5)E-05	1.5 (± 0.5)E-04	2.7 (± 0.5)E-04	2.6 (± 1)E-03
HC19	1.0 (± 0.5)E-04	1.8 (± 0.9)E-04	5.0 (± 3)E-04	7.5 (± 4)E-04
Average	1.4 (± 1)E-04	1.9 (± 0.5)E-04	4.0 (± 1)E-04	1.3 (± 0.9)E-03
Sagebrush				
HC16	1.6 (± 0.5)E-04	2.9 (± 2)E-05	2.4 (± 1)E-04	6.0 (± 2)E-03
HC17	2.7 (± 0.7)E-04	6.7 (± 3)E-05	2.1 (± 2)E-04	5.8 (± 4)E-03
HC18	4.2 (± 1)E-04	9.4 (± 3)E-05	2.7 (± 2)E-04	8.5 (± 5)E-03
HC19	9.3 (± 3)E-05	1.4 (± 0.3)E-04	5.7 (± 0.7)E-04	6.8 (± 3)E-03
Average	2.3 (± 1)E-04	8.0 (± 4)E-05	3.2 (± 2)E-04	6.8 (± 1)E-03
Short Needle Pine				
HC16	1.1 (± 0.8)E-04	1.0 (± 0.6)E-04	1.4 (± 1)E-04	2.0 (± 2)E-04
HC17	3.9 (± 0.5)E-04	1.9 (± 0.3)E-04	2.8 (± 0.6)E-04	3.9 (± 1)E-04
HC18	3.4 (± 1)E-04	1.3 (± 0.6)E-04	1.6 (± 0.9)E-04	9.1 (± 0.4)E-04
HC19	8.7 (± 3)E-05	1.7 (± 0.2)E-04	4.1 (± 0.4)E-04	4.3 (± 2)E-04
Average	2.3 (±2)E-04	1.5 (± 0.4)E-04	2.5 (± 1)E-04	4.8 (± 3)E-04
Tall Fescue				
HC16	5.4 (± 2)E-05	5.0 (± 2)E-06	4.1 (± 5)E-05	6.4 (± 5)E-04
HC17	4.5 (± 1)E-05	2.2 (± 0.5)E-05	2.2 (± 2)E-05	6.4 (± 6)E-04
HC18	9.8 (± 2)E-05	2.8 (± 2)E-05	4.4 (± 4)E-05	9.8 (± 7)E-04
HC19	8.7 (± 7)E-05	5.4 (± 4)E-05	2.5 (± 1)E-04	4.4 (± 3)E-04
Average	7.1(±3)E-05	2.8 (± 2)E-05	9.0 (± 10)E-05	6.8 (± 2)E-04
Burbank Soil				
HC16	2.3 (± 0.1)E-03	2.4 (± 0.6)E-04	7.1 (± 1)E-04	4.9 (± 1)E-03
HC17	3.4 (± 1)E-03	3.2 (± 1)E-04	ND	3.1 (± 1)E-03
HC18	1.5 (± 1)E-03	1.0 (± 0.6)E-03	ND	4.3 (± 2)E-03
Average	2.4 (± 1)E-03	5.3 (± 4)E-04		4.0 (± 0.9)E-03
Maxey Flats Soil				
HC16	2.6 (± 0.6)E-03	2.4 (± 0.8)E-04	2.1 (± 2)E-04	1.4 (± 0.2)E-03
HC17	3.3 (± 1)E-03	4.0 (± 0.7)E-04	ND	8.8 (± 3)E-04
HC18	4.9 (± 0.4)E-03	8.3 (± 0.1)E-04	2.8 (± 0.4)E-04	8.4 (± 1)E-04
Average	3.6 (± 1)E-03	4.9 (± 3)E-04	1.6 (± 1)E-04	1.0 (± 0.3)E-03

Although the deposition of aerosol materials to plant and soil surfaces may be a function of the relative humidity, in these experiments the residence time of the materials on the plant and soil surfaces should be completely independent of exposure conditions. This is because the plants and soil coupons were all held at the same temperature, light, and humidity conditions following exposure. The data presented in Table 3.25 show this to be generally true. For example, the half-lives for the chlorocarbons on the Ponderosa Pine foliage were relatively consistent (1 to 4 days) for all four compounds deposited under the different relative humidities. For the bush bean, the half-lives of three compounds were consistent to those for ponderosa pine, with the CCl_4 half-life showing a very large variance between experiments. In general, the half-lives for these compounds in sagebrush and short needle pine were similar to the other two species. In those casesin which the average half-life is higher, substantial variability does exist.

The CCl_4 proved to be the most difficult compound for reliable data because of its high volatility and background. It may be that a large portion of the CCl_4 was lost to evaporation before the plants could be sampled. The material that remained on the foliage surfaces may have been bound to adsorptive sites on dust particles, reducing the vapor pressure of the CCl_4. Under these circumstances the calculated half-lives may be artificially high. Overall, the data on the loss of C_2Cl_4 were the most consistent among the different plant species. The average calculated half-life for this compound on all plants was 3±1 days. For C_2Cl_6 the average half-live was 3±3 days, and for C_6Cl_6 was 5±6 days. These half-lives were measured on plants kept in the relatively still air (~0.5 mph) of the growth chambers. It is expected that these are worst-case estimates for the persistence of these compounds in the natural environment.

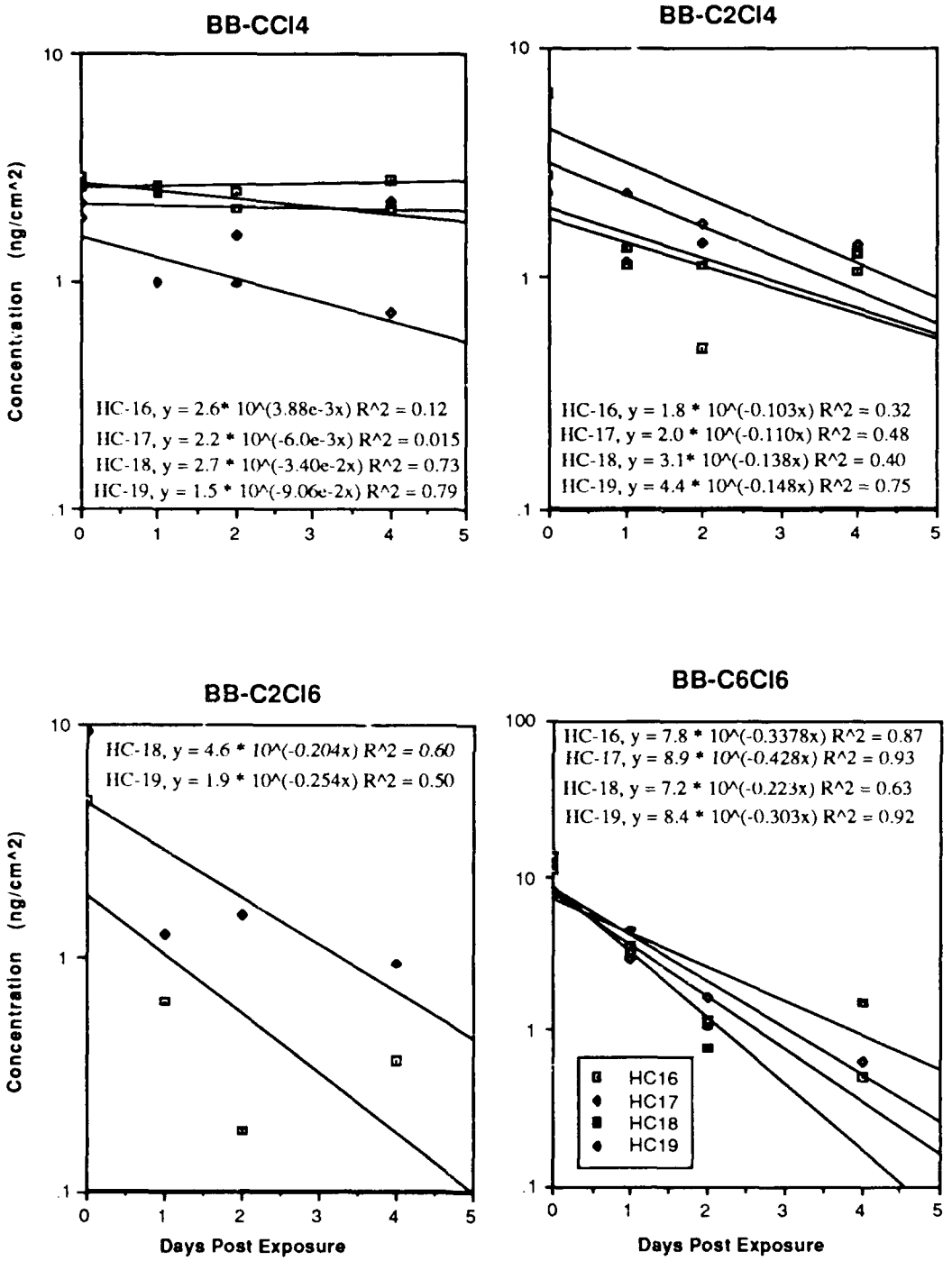


FIGURE 3.21. CONCENTRATION OF CHLOROCARBONS ON BUSH BEAN (BB) FOLIAGE FOLLOWING EXPOSURE TO HC SMOKE. THESE SAMPLES WERE COLLECTED FOLLOWING THE RELATIVE HUMIDITY TESTS

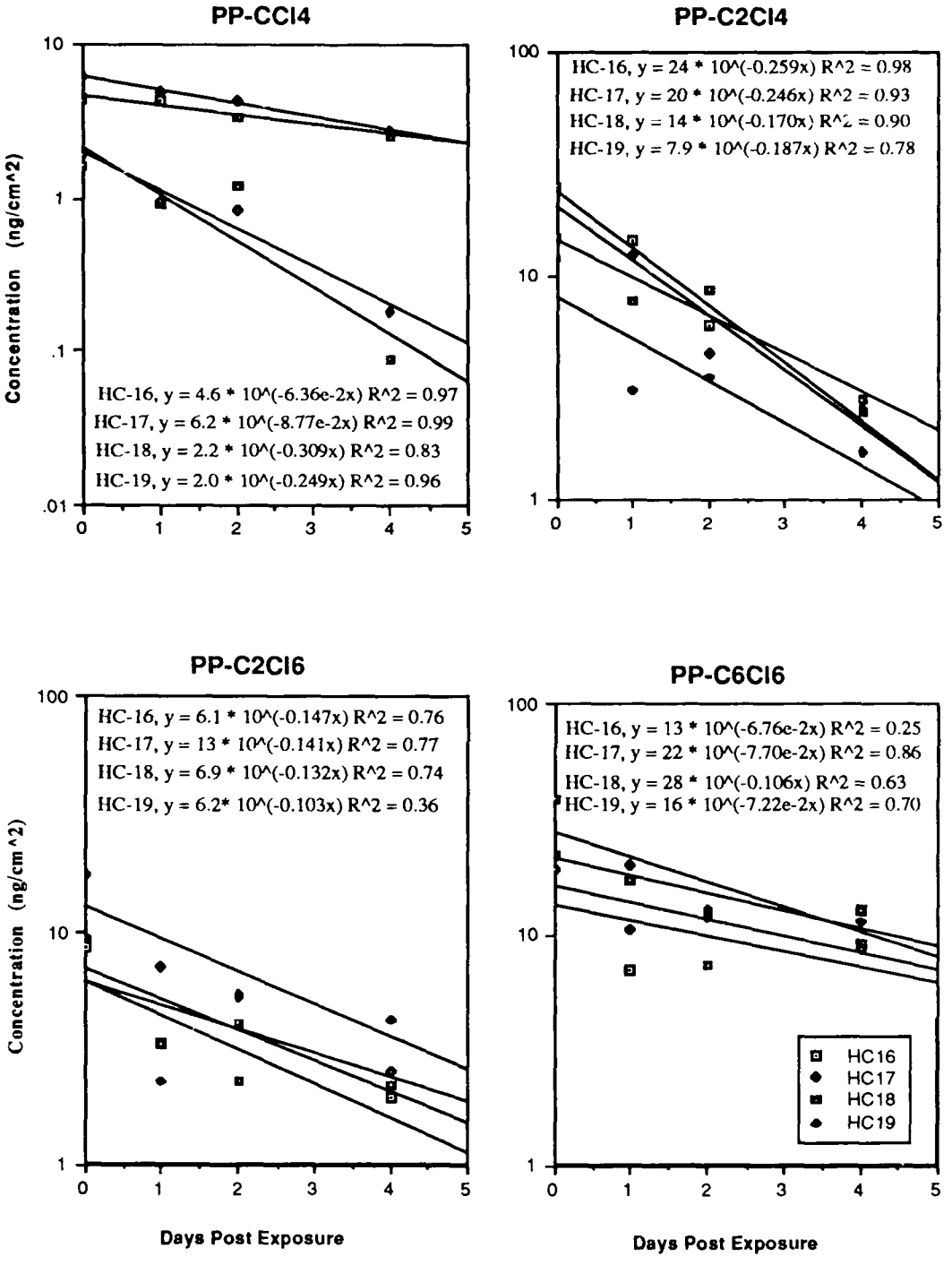


FIGURE 3.22. CONCENTRATION OF CHLOROCARBONS ON PONDEROSA PINE (PP) FOLIAGE FOLLOWING EXPOSURE TO HC SMOKE. THESE SAMPLES WERE COLLECTED FOLLOWING THE RELATIVE HUMIDITY TESTS

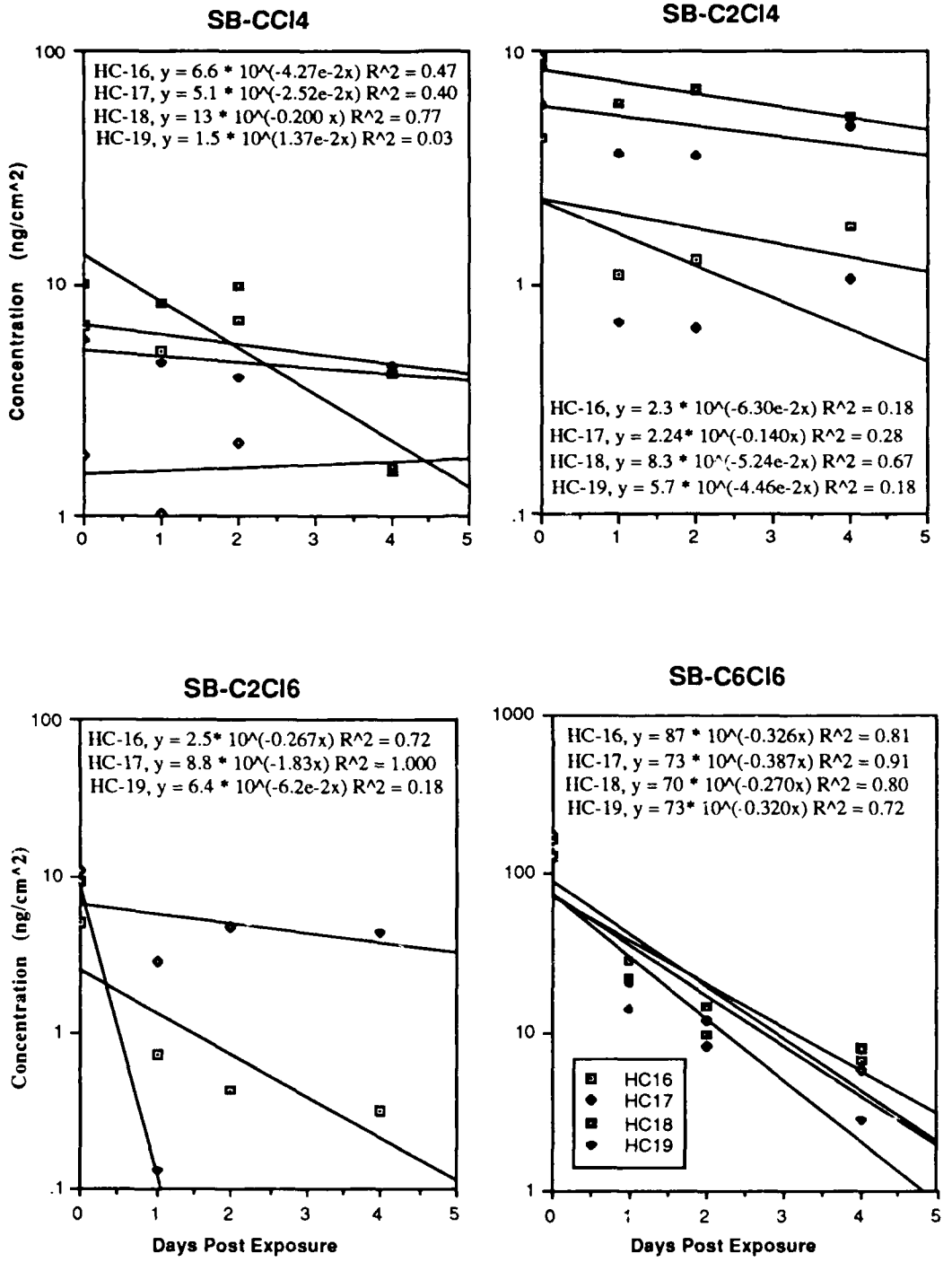


FIGURE 3.23. CONCENTRATION OF CHLOROCARBONS ON SAGEBRUSH (SB) FOLIAGE FOLLOWING EXPOSURE TO HC SMOKE. THESE SAMPLES WERE COLLECTED FOLLOWING THE RELATIVE HUMIDITY TESTS

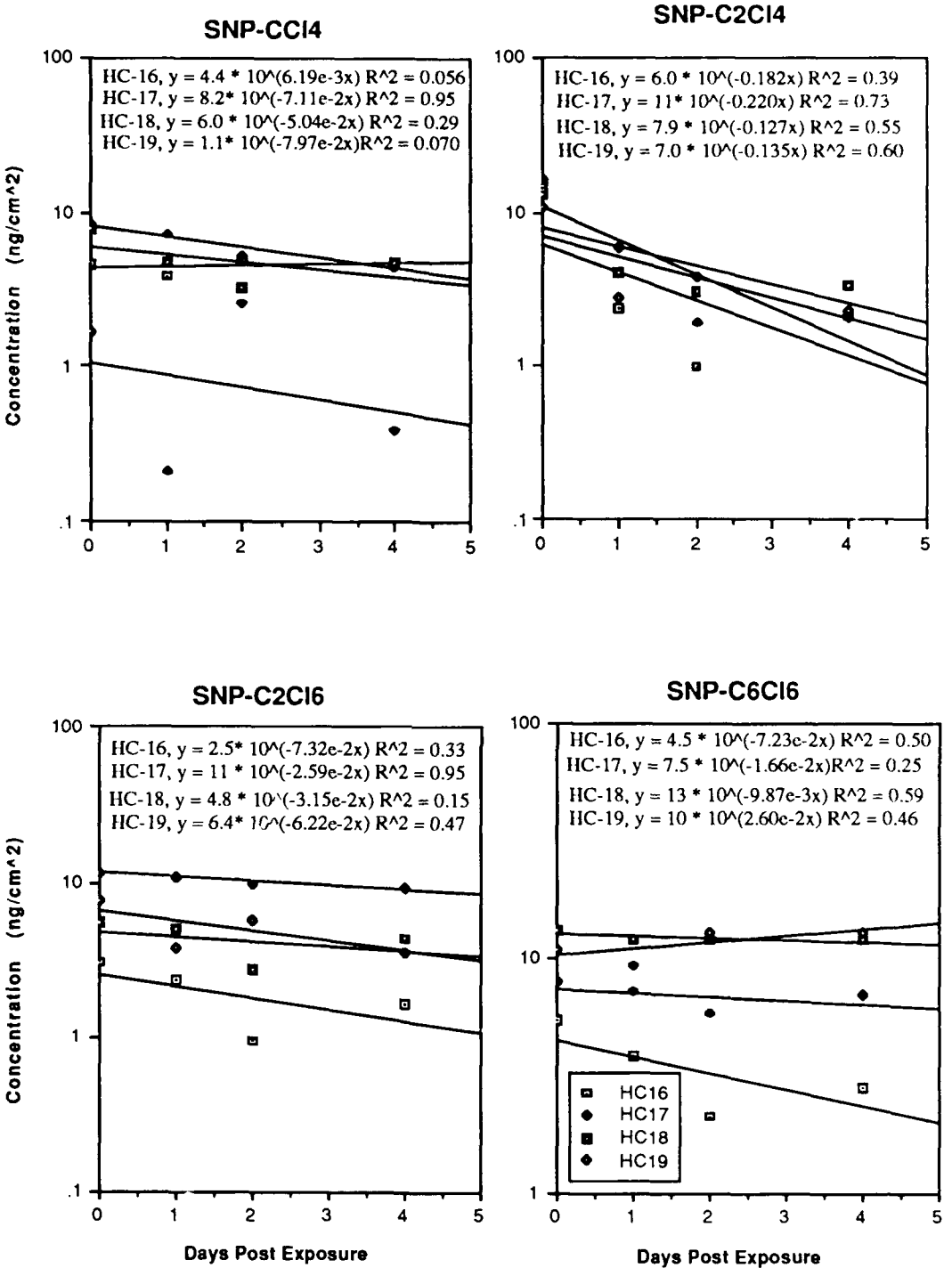


FIGURE 3.24. CONCENTRATION OF CHLOROCARBONS ON SHORT-NEEDLE PINE (SNP) FOLIAGE FOLLOWING EXPOSURE TO HC SMOKE. THESE SAMPLES WERE COLLECTED FOLLOWING THE RELATIVE HUMIDITY TESTS

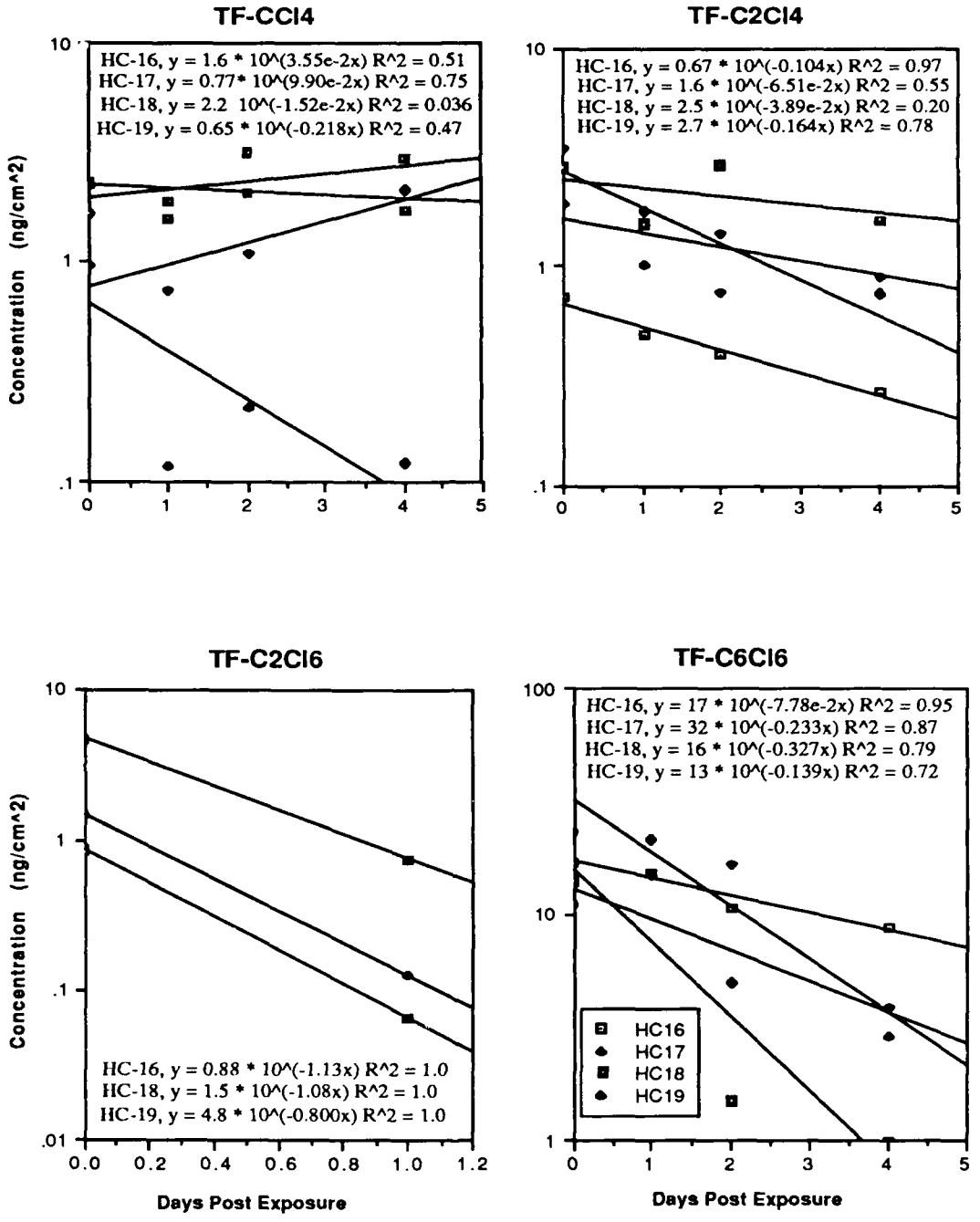


FIGURE 3.25. CONCENTRATION OF CHLOROCARBONS ON TALL FESCUE (TF) FOLIAGE FOLLOWING EXPOSURE TO HC SMOKE. THESE SAMPLES WERE COLLECTED FOLLOWING THE RELATIVE HUMIDITY TESTS

3.5.2 Persistence in Soil

The persistence of the chlorinated hydrocarbons was evaluated following airborne deposition of the compounds to soil surfaces. The loss of the chlorocarbons from the two test soils is depicted as a function of time in Figures 3.26 and 3.27. The soil deposition coupons were on exposed in HC-19 (first half, RH=55%, second half, RH=95%). There were insufficient data for the compound C_2Cl_6 to be contained in this analysis. It may be that C_2Cl_6 is transformed once adsorbed to the soils, or it is irreversibly bound by some mechanism.

The data obtained in the soil depuration experiments appear very noisy, with only two exponential regression fits giving R^2 values >0.6. Thus, based on the results, there is too little data to make a definitive observation comparing the depuration of the chlorocarbons from the two soils. The average half-life of CCl_4, C_2Cl_4 and C_6Cl_6 ranged from 7 to 50 days, somewhat longer than for foliar deposites. What is generally clear is that the residence time of these materials on the soil surfaces is extended as compared to the plant surfaces.

TABLE 3.25. APPARENT CHLOROCARBON HALF-LIVES DERIVED FROM THE SLOPES OF THE EXPONENTIAL RELATIONSHIP FIT TO THE DATA PRESENTED IN FIGURES 3.21-3.27

Experiment Code	Ponderosa Pine				Bush Bean			
	CCl_4	C_2Cl_4	C_2Cl_6	C_6Cl_6	CCl_4	C_2Cl_4	C_2Cl_6	C_6Cl_6
	(Half-Life in Days)				(Half-Life in Days)			
HC-16	4.7	1.2	2.1	4.5	78	3.0		0.89
HC-17	3.4	1.2	2.1	3.9	50	2.7		0.70
HC-18	0.97	1.8	2.3	2.8	8.9	2.2	1.5	1.4
HC-19	1.2	1.6	2.9	4.2	3.3	2.1	1.2	0.99
Average	2.6	1.4	2.6	3.8	35	2.5	1.3	0.98
Std. Dev.	2	0.3	0.4	0.7	30	0.4	0.2	0.3

Experiment Code	Sagebrush				Short-Needle Pine			
	CCl_4	C_2Cl_4	C_2Cl_6	C_6Cl_6	CCl_4	C_2Cl_4	C_2Cl_6	C_6Cl_6
	(Half-Life in Days)				(Half-Life in Days)			
HC-16	7.1	4.8	1.1	0.92	49	1.7	4.2	4.2
HC-17	12	2.2	0.16	0.78	4.2	1.4	12	18
HC-18	1.5	5.7		1.1	6.0	2.4	9.6	31
HC-19	22	6.8	4.9	0.94	3.8	2.2	4.8	12
Average	11	4.7	2.1	0.94	16	1.9	7.6	16
Std. Dev.	9	2	2	0.1	20	0.5	4	10

Experiment Code	Tall Fescue				Burbank Soil			Maxey Flats Soil		
	CCl_4	C_2Cl_4	C_2Cl_6	C_6Cl_6	CCl_4	C_2Cl_4	C_2Cl_6	CCl_4	C_2Cl_4	C_2Cl_6
	(Half-Life in Days)				(Half-Life in Day)			(Half-Life in Days)		
HC-16	8.5	2.9	0.27	3.9	64	15	21		12	6.8
HC-17	3.0	4.6		1.3		2.5	3.6	22	72	
HC-18	19	7.7	0.28	0.92	35	5.3	12	20	4.9	
HC-19	1.4	1.8	0.38	2.2						
Average	8.2	4.3	0.31	2.1	50	7.7	12	21	30	6.8
Std. Dev.	8	3	0.06	1	20	7	9	1	40	

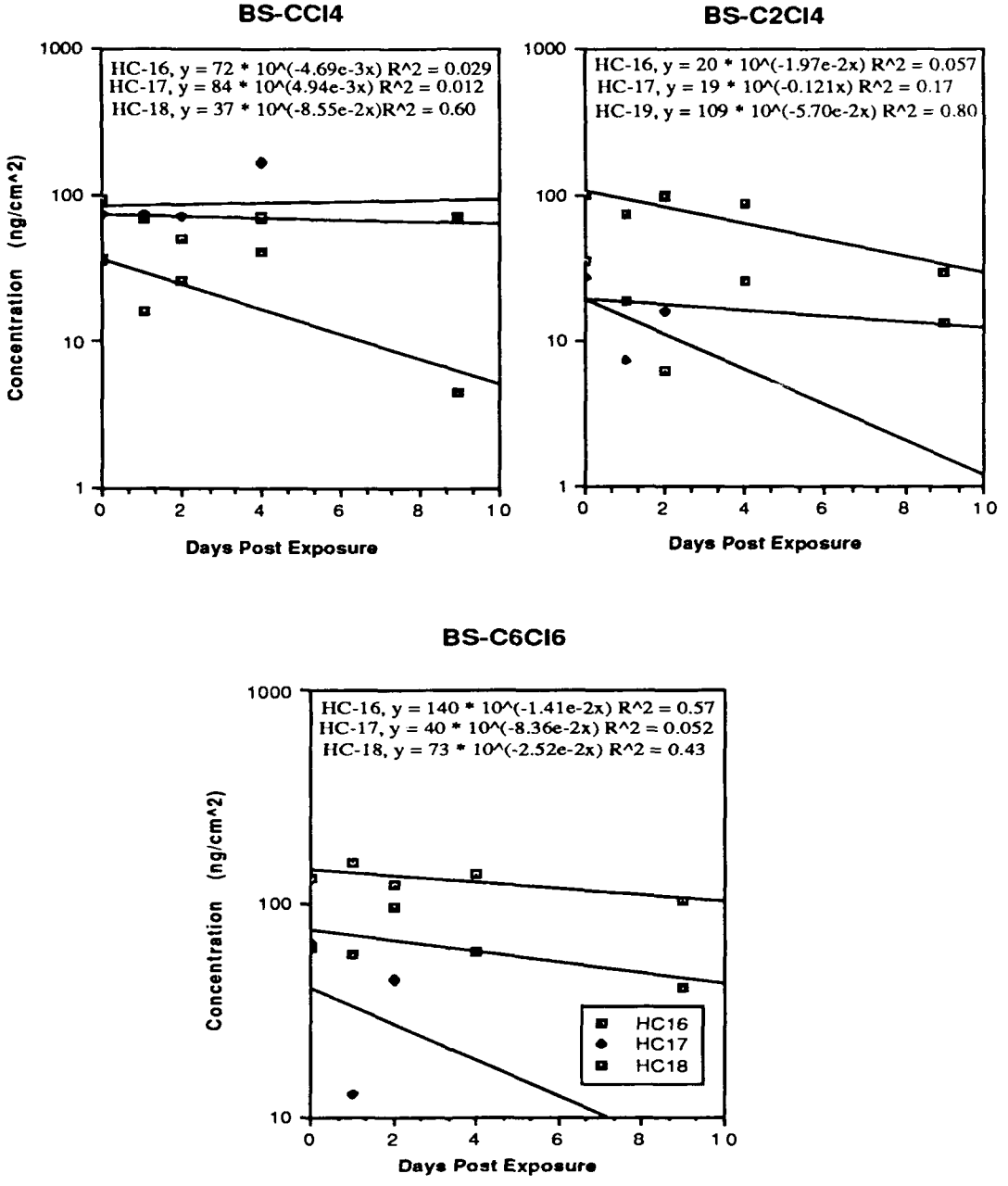


FIGURE 3.26. CONCENTRATION OF CHLOROCARBONS ON BURBANK SOIL (BS) SURFACE FOLLOWING EXPOSURE TO HC SMOKE. THESE SAMPLES WERE COLLECTED FOLLOWING THE RELATIVE HUMIDITY TESTS. THE SOIL COUPONS WERE NOT EXPOSED TO THE RAINOUT CONDITIONS USED IN HC-19

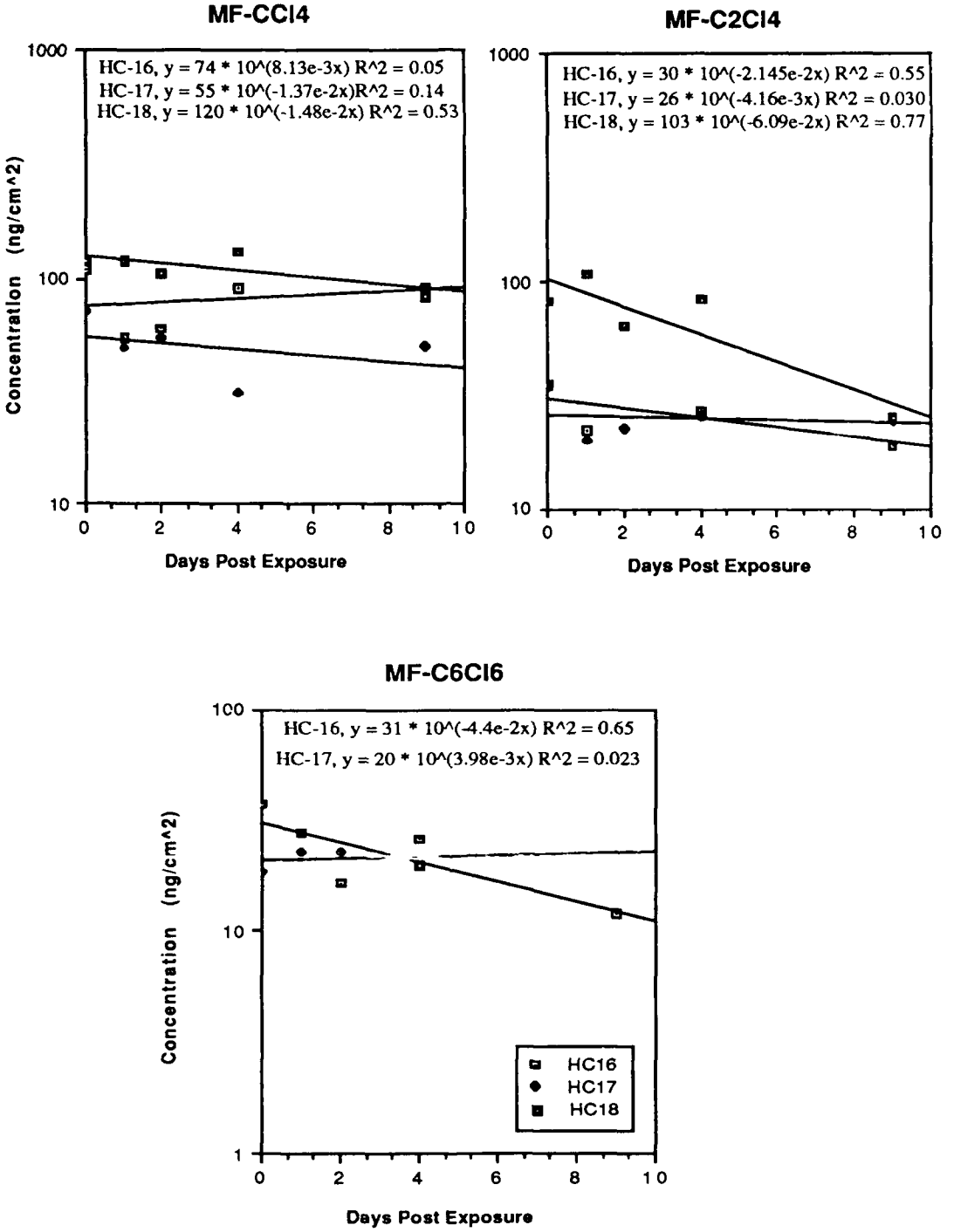


FIGURE 3.27. CONCENTRATION OF CHLOROCARBONS ON MAXEY FLATS SOIL (MF) SURFACE FOLLOWING EXPOSURE TO HC SMOKE. THESE SAMPLES WERE COLLECTED FOLLOWING THE REALTIVE HUMIDITY TESTS. THE SOUL COUPONS WERE NOT EXPOSED TO THE RAINOUT CONDITIONS USED IN HC-19

3.6 PHYTOTOXICITY: TERRESTRIAL PLANTS

3.6.1 Mass Loading, Deposition Velocities, and Retention of Inorganic HC Smoke Constituents Deposited to Foliar Surfaces

Range-Finding Series. The RFT involved exposure of plants and soils to HC smokes for 1, 2, 3 and 4 h; smoke concentrations in air were 410, 480, 380, and 450 mg/m^3, respectively. Exposures were conducted at 2 mph, 40 to 45% RH, and a temperature of 22°C. Analyzed Zn concentrations in air were approximately constant at 25% of the total HC air concentration, and were 97, 110, 89, and 110 mg/m^3, respectively. Zn represents approximately 25% of the total HC mass of aerosolized samples. All subsequent mass loading (ML) and deposition velocity (V_d) calculations are based on Zn. Selection of Zn as the quantitative indicator is based on uncertainties as to the persistence of the major organic constituents of HC smokes, once deposited to foliage and/or soils. Similarly, Al was evaluated in the RFT as an indicator of dose, but its concentration in smoke compared to control leachates of soils and plants made it unsuitable because of high background concentrations.

Mass loading and foliar retention data for the Zn component of HC smoke are shown in Table 3.26. Foliar mass loading for the four plant species ranged from 2 to 16 μg Zn/cm^2 foliage for the 1- to 4-h exposures. Mass loading to foliage of ponderosa pine and sagebrush was approximately twice that observed for bushbean and tall fescue, and proportional to exposure duration. This difference may have been caused in part by both the taller stature of these plants (pine and sagebrush) as well as their elongated needles which project into the windstream and may have promoted greater turbulence and therefore deposition to the needle surfaces.

Application of a postexposure simulated rainfall resulted in a substantial removal of foliar contaminants. Overall, 50% to 85% of the foliar-deposited Zn was removed in the leaching process. Leaching was least effective in removing contaminants from sagebrush, which was probably the result of the plant's complex cuticular structure (Van Voris et al. 1987). In each of the other three species, except for pine, there appears to be a definite relationship between exposure duration and/or mass loading on foliar retention. In each instance, retention of HC smoke-derived Zn increases with length of exposure. It is unlikely that this is caused by the mass of Zn, since the number of sorption sites is constant. Instead, increased exposure duration may have permitted deeper penetration of aerosols into the physical cuticular structure, making available more exchange surface that may not be readily available for leaching. This may result from processes such as foliar absorption and/or diffusion.

TABLE 3.26. FOLIAR MASS LOADING AND LEACHABILITY OF THE Zn FRACTION OF HC SMOKES FOLLOWING 1, 2, 3, AND 4 H OF EXPOSURE (RFT) [a]

Plant Species	Exposure Duration (h)	Foliar Mass Loading (μg Zn/cm^2 ±S.D., N=3)	Foliar Retention[b] (%)
Ponderosa Pine	1	3.25±0.60	24±9
	2	7.62±1.10	18±1
	3	10.49±1.43	20±5
	4	16.23±2.84	28±5
Sagebrush	1	4.53±1.32	39±1
	2	9.43±1.33	27±4
	3	11.38±2.06	45±6
	4	16.70±2.33	34±10
Bushbean	1	2.07±0.49	18±2
	2	5.62±1.88	14±3
	3	4.37±0.90	26±4
	4	7.74±1.92	48±1
Tall Fescue	1	2.19±0.62	11±4
	2	4.40±1.42	14±1
	3	5.80±0.61	30±1
	4	8.39±1.54	31±5

(a) Plants exposed to HC smokes for 1, 2, 3, and 4 h; total smoke concentrations in air were 410, 480, 380, and 450 mg/m^3, respectively (MMAD and GSD were 1.9±1.5). Exposures were conducted at 2 mph, 40 to 45% RH, and a temperature of 22°C. Analyzed Zn concentrations in air are approximately constant at 25% of the total HC air concentration, and were 97, 110, 89, and 110 mg Zn/m^3, respectively.

(b) Postexposure leaching/simulated rainfall was conducted within 2 h of contamination, and consisted of 350 mL of synthetic rainwater passed through the canopy over a 15-min period, equivalent to a 0.5-cm rainfall.

Deposition velocities (V_d), which are routinely computed for experimental exposures, provide a basis for estimating the transfer of smoke constituents from air to foliar and/or soil surfaces. This parameter, once established, can be used to estimate foliar or soil mass loading and thus projected damage under field conditions, given air concentration, wind speed, and relative humidity (if effective in altering particle size distributions for a particular smoke).

Deposition velocities (V_d) for individual plant species were independent of exposure duration (Table 3.27), as would be expected. Values of V_d for ponderosa pine and sagebrush are 0.010 and 0.012 cm/s, respectively. Collection efficiency of tall fescue and bushbean is less, with V_d values of approximately 0.0058 cm/sec. These values are very similar to those for RP/BR smokes of similar MMAD and GSD (Van Voris et al. 1987).

TABLE 3.27. FOLIAR DEPOSITION VELOCITIES FOR THE Zn COMPONENT OF HC SMOKE AS A FUNCTION OF EXPOSURE DURATION (RFT)

Plant Species	Exposure Duration (h) 1	2	3	4	Average V_d
			(cm/s x 10^3)		
Ponderosa Pine	9.3±1.7	9.6±1.4	10.9±1.5	10.5±1.8	10.1
Sagebrush	13.0±3.8	11.9±1.7	11.8±2.1	10.8±1.5	11
Tall Fescue	6.3±1.8	5.6±1.8	6.0±0.6	5.4±1.2	5.8
Bushbean	6.9±1.4	7.1±2.4	4.6±0.9	5.0±1.2	5.9

Wind Speed Series. In the wind speed test series, both plants and soils were exposed to HC smokes at wind speeds of 2 to 10 mph. Relative humidity ranged from 50% to 70% for the four exposures; exposure duration was 2 h. Smoke concentrations for the four exposures were 260, 370, 420 and 340 mg HC/m^3, with calculated Zn concentrations of 66.5, 94.7, 89.9, and 78.2 mg Zn/m^3 respectively.

As observed previously with RP/WP and fog oil smokes (Van Voris et al. 1987; Cataldo et al. 1988), mass loading to foliar surfaces of each of the five plant species increased with increasing wind speed (Table 3.28). Mass loading of Zn increased by a factor of 36, 16, 12, 3, and 13 for ponderosa pine, short-needle pine, sagebrush, tall fescue, and bushbean, respectively, between 2 mph and 10 mph.

This large increase however, is substantially less than that observed previously for ponderosa pine and grasses exposed to the RP and WP smokes. There are two possible explanations for this observation. First, particle size distribution is significantly lower for HC (1.5 to 1.6 µm) compared to phosphorus smokes (Van Voris et al. 1987; 1.7 µm), and as such particle momentum at the higher wind speeds may be insufficient to significantly affect penetration of the foliar boundary layers and thus deposition to foliage. Second, the composition of HC particles, namely degree of hydration, may influence the extent of particle retention or bounce off of foliar surfaces following impaction.

TABLE 3.28. INFLUENCE OF WIND SPEED ON MASS LOADING AND DEPOSITION VELOCITY OF HC SMOKES TO FOLIAR SURFACES, AND EXTENT OF FOLIAR RETENTION OF Zn FOLLOWING SIMULATED RAINFALL

Plant species/ Wind speed (mph)	Mass loading ($\mu g\ Zn/cm^2$)	Foliar retention (% retained)	Deposition velocity ($cm/s \times 10^3$)
Ponderosa Pine			
2	4.43±0.72	19.7±12.6	9.2±1.5
4	12.21±3.54	18.5±6.6	17.8±5.2
6	16.69±9.17	35.8±12.8	25.8±14.2
10	143.50±95.27	17.6±12.7	254.8±169.2
Short Needle Pine			
2	5.9±1.33	6.0±3.8	12.4±2.8
4	10.29±1.81	15.1±8.5	15.0±2.6
6	11.9±54.86	7.9±2.6	18.5±7.5
10	88.96±52.96	4.4±2.4	158.0±94.1
Sagebrush			
2	5.67±1.26	8.1±2.6	11.8±2.6
4	16.50±6.84	28.6±6.1	24.0±9.9
6	21.42±10.46	27.0±15.8	33.1±16.2
10	72.03±47.66	46.3±29.1	127.9±84.7
Tall Fescue			
2	2.69±0.43	23.4±6.9	5.6±0.9
4	5.82±0.76	16.6±11.0	8.5±1.1
6	4.84±0.92	12.1±3.6	7.5±1.4
10	9.70±0.99	23.2±6.6	17.2±1.8
Bushbean			
2	4.14±1.40	20.8±10.8	8.6±2.9
4	7.25±1.48	47.2±14.0	10.5±2.1
6	13.67±3.23	22.9±10.7	21.1±5.0
10	51.03±16.83	58.1±27.4	90.6±29.9

Results for foliar mass loading, retention following postexposure simulated rainfall, mass loading during rainout and deposition velocities (V_d) for the five plant species are shown in Table 3.28. Values shown for V_d, describe the comparative collection efficiency for the five plant species.

Two basic processes may be impacted and influence the effects of obscurant smokes through a postexposure leaching. The first process, namely solubilization and removal of foliar

deposited smoke components, would lower the overall foliar dose, limit the total toxicant being absorbed through the cuticle, and thus ameliorate the effects of the smoke. Alternatively, the presence of excess foliar surface moisture may accelerate the foliar absorption of toxic contaminants, intensifying the toxicity response.

The foliar retention data shown in Table 3.28 indicate that, for a specific plant species, there is no significant change in the leachability of foliar deposits with increasing mass loading (i.e., wind speed), except for sagebrush where entrainment may play a role. This behavior is comparable to results obtained for red phosphorus, white phosphorus, and fog oil.

Overall retention following simulated rainfall does vary with plant species. Retention averages approximately 20% to 30% for ponderosa pine, sagebrush, tall fescue, and bushbean, and approximately 9% for short-needle pine. These patterns are, again, quite comparable to that observed for the phosphorus smokes, and reflect the relative effectiveness of impinging water droplets on accessing and displacing foliar contaminants.

Deposition velocities (V_d), which are routinely computed for experimental exposures, provide a basis for estimating the transfer of smoke constituents from air to foliar and/or soil surfaces. The V_d values for the HC-WST series are shown in Table 3.29. With the exception of tall fescue, V_d values increase with increasing wind speed, particularly between 6 mph and 10 mph. Between 2 mph and 10 mph, V_d increases by a factor of 10 to 15 for the other species. It should be noted that values of V_d for the 2-mph treatments are approximately comparable to that observed for the other obscurant smokes, while the magnitude of increase between 2 mph and 10 mph is substantially less. For the phosphorus smokes, V_d increased from approximately 8 to 800 x 10^3 cm/s.

Relative Humidity Tests. The RHT series for HC smokes involved exposure of both plant canopies and soils to hexachloroethane aerosols with relative humidities maintained at 20 (HC-16), 55 (HC-17), and 85% (HC-18). In addition, HC deposition and impacts were determined under simulated rainout conditions (HC-19); this involved 2-h exposure to smokes at 55% RH, followed by an additional 2 h of aerosol exposure under simulated rainfall. Wind speed was maintained at 2 mph for all tests; smoke concentrations, corrected for moisture were 460, 450, 320 and 460 mg/m^3 for HC-16 through HC-19, respectively. All effects data are compared using the Zn component of HC smokes, which amounts to approximately 25% of the total smoke mass, as the basis for dose.

Results for foliar mass loading, retention following postexposure simulated rainfall, mass loading during rainout, and deposition velocities (V_d) for the five plant species are shown in Table 3.29. Values shown for V_d, describe the comparative collection efficiency for the five

plant canopies, and the influence of relative humidity deposition of aerosils to plant canopies. As noted in previous studies, V_d values provide the only basis for comparing plant canopy types and the impacts of treatments, because experimental variables such as air concentration and exposure duration are normalized. From the data presented, deposition or collection efficiency is generally comparable for all five plant species at 20 and 55% RH. At 85% RH, there is a marked increase in V_d for all species. This most likely results form the small increase in MMAD of particles at the higher RH (see Table 3.3).

Overall, mass loading rates are comparable for ponderosa pine, short-needle pine and sagebrush, and slightly less for tall fescue and bushbean. Application of a postexposure simulated rainfall shows retention to vary with plant species as noted in previous experiments. The highest foliar retention values (generally >40%) are obtained with ponderosa pine, sagebrush, and bushbean, and substantially less with short-needle pine and tall fescue (<16%). The foliar retention data, although exhibiting a rather large variability, would indicate that Zn, in several of the plant species, is not readily leachable, and thus is either bound to exchange sites on foliar surfaces or is being absorbed into the leaves. The differences observed with plant species, and the fact that the complexity of cuticle surface morphology and canopy structure does not correlate with retention, would support the contention that retention results from sorption or absorption differences between plant species. There is no indication that RH plays a significant role in foliar retention.

In the rainout treatment, foliar mass loading was substantially reduced for the pines and tall fescue compared to the RH treatments, and nearly the same as the RH treatments for bushbean and sagebrush. Again, this would support the contention that these two plant species may have a higher sorptive or absorptive capacity for Zn than the pines or grass species.

Cumulative Dose Test Series. In the cumulative dose tests (CDT) series, plants were exposed nine times over a 3-week period. Two concentrations of HC were targeted and achieved for each exposure, a low-concentration of 120±18 mg/m^2 and a high concentration of 600±90 mg/m^2. Three plants of each species were used for the two concentrations over the nine exposures. The results of foliar mass loading analysis (based on µg Zn/cm^2) are shown in Table 3.30.

TABLE 3.29. INFLUENCE OF RELATIVE HUMIDITY AND SIMULATED RAINOUT, AND POST-EXPOSURE SIMULATED RAINFALL ON FOLIAR MASS LOADING AND DEPOSITION VELOCITY

Plant Species/ Treatment	Mass Loading[a] ($\mu g\ Zn/cm^2$)	Foliar Retention[b] (% retained)	Deposition Velocity[c] ($cm/s \times 10^3$)
Ponderosa Pine			
20% RH	11.51±3.11	37±20	6.7±1.8
55% RH	17.79±4.50	18±12	8.8±2.2
85% RH	18.53±4.86	40±10	10.7±2.8
Rainout	4.79±1.42	na	na
Short-Needle Pine			
20% RH	10.17±1.85	14±10	5.9±1.1
55% RH	10.29±2.28	16±9	5.1±1.1
85% RH	21.33±2.91	11±3	7.2±1.4
Rainout	5.16±2.11	na	na
Tall Fescue			
20% RH	6.78±2.17	6±4	3.9±1.3
55% RH	10.29±2.28	16±9	5.1±1.1
85% RH	12.38±2.50	11±3	7.2±1.4
Rainout	2.11±0.96	na	na
Bushbean			
20% RH	9.82±2.94	35±18	5.7±1.7
55% RH	11.47±2.17	51±20	5.7±1.1
85% RH	14.65±3.51	30±6	8.5±2.0
Rainout	10.39±3.25	na	na
Sagebrush			
20% RH	15.62±4.47	44±9	9.0±2.6
55% RH	15.09±4.88	67±18	7.5±2.4
85% RH	17.80±3.75	47±13	10.3±2.1
Rainout	13.80±3.25	na	na

(a) Avg±S.D., n=10.
(b) Foliar retention calculated based on mass loading before and after a simulated rainfall of 0.5 cm. Avg±S.D., n=4; na, not applicable.
(c) Avg±S.D., n=10; na, not applicable.
(d) Plants exposed to HC aerosols for 120-min at 55% RH, followed by 120-min exposure to the same aerosols under simulated rainout conditions.

TABLE 3.30. FOLIAR MASS LOADING OF THE Zn FRACTION OF HC SMOKES FOLLOWING CUMULATIVE DOSE EXPOSURES(a)

Plant species	Mass Loading (μg Zn/cm^2) Low concentration ±S.D.	High concentration ±S.D.
Bush bean	4.09±0.5	8.21±3.37 (b)
Sagebrush	18.20±9.56	163.33±35.1
Short-needle pine	15.13±3.62	72.32±11.462
Tall fescue	5.65±0.46	29.33±8.93
Ponderosa pine	13.45±1.27	75.68±14.61

(a) Plants were exposed nine times for 2 h each exposure; total smoke concentrations in the air were approximately 120 and 600 mg/m^2 for the low and high-concentration runs, respectively. Exposures were conducted at 2 mph, 40% to 45% RH, and a temperature of 22°C.
(b) Bush beans were terminated after two exposures in the high-concentration runs. Two of the three short-needle pines were terminated after seven of the high-concentration runs.

To properly interpret the foliar mass loading data given in Table 3.30, it must be noted that some of the plants were terminated prematurely when severe phytotoxic effects became evident (cf. Section 3.6.3 below). These effects were most apparent in all the high-concentration bush bean treatments and two of the high-concentration short-needle pine treatments. These plants were terminated after three and eight exposures, respectively. An additional set of three bush beans were substituted for the original high-concentration plants beginning with the sixth exposure. However, these plants also exhibited severe symptoms after only two exposures and were again terminated early. Thus, premature termination of these bush beans accounts for the lower mass loading concentrations observed in the high-concentration exposures, only twice that of the low concentrations.

Mass loading values for the short-needle pine, tall fescue, and ponderosa pine were approximately five times higher in the high-concentration exposures, reflecting the fivefold concentration difference in the smoke. Sagebrush however, exhibited a ninefold increase in the high-concentration plants. This may be a result of anatomical factors such as leaf morphology, surface hairs, and cuticular wax.

The mass loading concentrations in Table 3.30 for both the high and low exposures for the other four species are somewhat lower than would be expected following a total of 18 h of exposure if the deposition patterns observed in the earlier rangefinding tests were to continue. Rough calculations based on a 25% Zn concentration in the HC smoke aerosol would indicate an average exposure of 30 mg Zn/m^3 per run for the low-concentration and 150 mg Zn/m^3 for the high-dose exposures. Previous foliar mass loadings of the Zn fraction

of HC given in Table 3.26 for the five plant species was 4 to 10 μg Zn/cm^2 for a 2-h exposure to HC air concentrations comparable to the CDT low-dose level. Assuming nine consecutive dosings, mass loading for the low-dose CDT should approximate 36 to 90 μg Zn/cm^2. The data actually obtained for the low-dose CDT series shown in Table 3.30 are substantially lower than expected in these measurements. Similarly, the reported mass loadings for the high dose treatments ranged from 8 to 163 μg/cm^2, and were lower than anticipated for nine consecutive exposures.

These apparent discrepancies may have been caused by possible resuspension or loss of the HC from the leaf surface due to handling (transfer to and from wind tunnel and growth chamber, watering, gas exchange measurements) between the nine separate exposures or, more likely, foliar absorption of significant amounts of the Zn by the plant over the longer experimental period (19 days).

3.6.2 Mass Loading and Deposition Velocities for Soil Surfaces

In the initial range-finding (RFT) exposure series, two soil types were exposed to HC smokes for 1 to 4 h. Mass loading rates varied markedly for the two soils (Table 3.31), averaging 0.37 and 6.37 μg Zn/cm^2/h for Burbank and Maxey Flat soil, respectively. Deposition velocities for the two soils were 0.0011 and 0.0189 cm/s, respectively. It is unclear as to why deposition varies with these two soil types, since sedimentation controls deposition; it is likely that Zn extractions were not effective (see p. 3.42 and Figure 3.19). This difference for soil deposition was not observed for either the RP, WP, or fog oil exposures. Physical placement within the tunnel (upwind of plant canopies), soil moisture levels, surface texture, and particle distributions for aerosols were similar. A potential irreversible binding (not extractable with 0.01 N HNO_3) of the Zn to the soil particles by the Burbank soil may therefore account for some of these results.

Wind Speed Tests. As noted (Table 3.31), mass loading rates and V_d values for soils are substantially different from those previously observed for the phosphorus and fog oil smoke RFT series (Van Voris et al. 1987; Cataldo et al. 1988). The HC deposition results for the WST series, tabulated in Table 3.32, for the two soil types also show several interesting trends. The deposition velocities for the 2-mph treatment are generally comparable to those observed for the phosphorus smokes, while V_d values for both soils are relatively constant for wind speeds of 2 to 4 mph with only minor increases observed for the 6- and 10-mph exposures. This is markedly different than observed previously (Van Voris et al. 1987; Cataldo et al. 1988). Also, the overall higher deposition of Zn to the clay compared to silt-sand soil is difficult to interpret. While reported values are corrected for background Zn,

TABLE 3.31. MASS LOADING (μg Zn/cm^2) AND DEPOSITION VELOCITIES (cm/s x 10^3) TO SOIL FOR THE Zn COMPONENT OF HC SMOKE AS A FUNCTION OF EXPOSURE DURATION (RFT)

Soil Type/ Exposure (h)	Mass Loading (μg Zn/cm^2)	Deposition Velocity (cm/s x 10^3)
Burbank silt-sand		
1	0.38±0.12	1.20±0.40
2	0.43±0.26	0.60±0.30
3	0.98±0.40	1.00±0.40
4	2.26±0.76	1.50±0.50
Maxey Flats clay		
1	9.78±0.25	30.30±0.70
2	10.56±5.01	14.30±6.30
3	16.24±2.22	17.70±2.30
4	20.12±1.20	13.50±0.80

TABLE 3.32. INFLUENCE OF WIND SPEED ON MASS LOADING AND DEPOSITION VELOCITIES OF HC SMOKES TO SOIL SURFACES

Soil Type/ Wind Speed	Mass Loading (μg Zn/cm^2)	Deposition Velocity (cm/s x 10^3)
Burbank silt-sand		
2 mph	1.63±0.22	2.5±0.3
4 mph	3.86±2.07	6.9±3.7
6 mph	4.75±1.18	9.9±2.5
10 mph	6.60±1.25	9.6±1.8
Maxey Flats clay		
2 mph	7.55±1.39	11.7±2.1
4 mph	6.20±0.25	11.0±0.4
6 mph	8.90±0.91	18.6±1.9
10 mph	13.70±0.4	19.9±0.6

which was acid extracted, it is again possible that in the silt-sand Zn may be irreversibly bound and not extractable using the present method.

Relative Humidity Test Series. While the wind speed was maintained at 2 mph during these experiments, the mass loading and deposition velocities of the 20% and 55% RH exposures (Table 3.33) more closely approximated those of the previous 4-mph exposures (Table 3.32) and are much higher than the 4-h range-finding series (Table 3.31). At constant wind speeds these are a direct reflection of the aerosol mass concentrations of each experiment where the ranges for all the RH series were higher than the first three of the RFT series. The actual fresh concentration were 530, 680, 1280, and 850 mg/m^3 (Zn concentration of 130, 160, 130, and 160 mg/m^3) for the 25%, 55%, 85%, and rainout exposures, respectively. Evidence of soil type differences is not seen in the two lower RH exposures but is seen in the 85% exposure. There was no reasonable explanation for this occurrence. The aerosol mass concentration of the 85% RH exposure was also slightly lower although the soil mass loading was elevated, indicating a possible humidity interaction in this case as well.

TABLE 3.33. INFLUENCE OF RELATIVE HUMIDITY ON MASS LOADING AND DEPOSITION VELOCITIES OF HC SMOKES ON SOIL SURFACES

Soil Type/ % Relative Humidity	Mass Loading (μg Zn/cm^2±SD; N=3)	Deposition Velocity (cm/s x 10^3 ±SD; N=3)
Burbank		
20%	6.31±1.44	3.65±0.94
55%	5.92±1.57	2.94±0.85
85%	7.24±3.71	4.19±2.02
Maxey Flats		
20%	5.28±2.13	3.05±1.55
55%	5.24±2.39	2.60±0.58
85%	15.79±2.01	9.13±2.30

Cumulative Dose Series. While V_d calculations were not possible given the nature of nine successive exposures in the CDT series, mass loadings to the soils were within that expected from the RFT series (Table 3.34). There was again an apparent difference between the two soil types comparable to that seen in all previous exposure series. Again, no explanation is can be provided.

TABLE 3.34. INFLUENCE OF CUMULATIVE DOSE EXPERIMENTS ON MASS LOADING OF HC SMOKES ON SOIL SURFACES

Soil Type/ Dose Rate	Mass Loading ($\mu g\ Zn/cm^2 \pm SD$; N=3)
Burbank	
Low	15.39±1.17
High	117.71±12.34
Maxey Flats	
Low	23.31±2.15
High	167.89±6.46

3.6.3 Phytotoxicity of HC Smokes Deposited to Foliar Surfaces

Foliar Contact Toxicity

The previous studies were performed to establish the relative importance of several environmental and exposure conditions on the deposition of HC smokes to foliar surfaces. These included exposure duration, RH, windspeed, and repeated exposures. Each of these parameters may have an influence on the mass loading of smokes to vegetative (foliar) surfaces. In the following studies we have attempted to establish the relationship between foliar mass loading and phytotoxicity arising from direct contact with foliage. Each of these studies involves bagging of the soil container to prevent contamination, thus allowing evaluation of only contact toxicity. The indirect effects of HC smoke on plants, via soil contamination, is addressed in a later section.

Dealing with foliar contact toxicity problems presents several problems. First, in the present study three of the five plant species are natural genetic stock, and each individual can represent a slightly different genotype. This allows for some physiological variability and possible toxicity response differences within each test species. Second, under both field conditions and in the wind tunnel exposure system, where air movement occurs along a given vector (ie., wind direction), deposition to canopies can occur irregularly depending on canopy structure, density, and the presence of back eddies. These air movements and currents account for a substantial fraction of the foliar deposition in both instances, and are representative of real world conditions. This approach is substantially more suited to toxicity testing than stirred or unstirred static exposure systems. The third problem, assuming natural variability in test species and foliar deposition patterns, is how to quantitate damage to

vegetation in a consistent and cost-effective manner. After preliminary results with RP smokes (Van Voris et al. 1987) were obtained, it was decided that the best approach to evaluating contact toxicity was to use a nonparametric grading system, namely, a modification of the Daubenmire (1959) rating scale as a damage index.

The modified Daubenmire rating scale (MDRS) and descriptors for toxicity symptoms, are given in Table 2.6, are used to describe the toxicity responses in each of the following studies. The MDRS is used to describe the extent of visual damage caused by the HC smoke delivered under different experimental conditions. This can be any one, or more, of the listed symptoms; however, for the HC smoke the major effects appeared to be tip burn and chlorosis. In the case of the pines, grass, and in some instances, sagebrush, the intensity of foliar damage was further quantitated by determination of the physical length of needle or leaf damage. It should be restated that the data generated for foliar contact toxicity are nonparametric, and represent an estimate of foliar damage. The physiological data (photosynthesis and respiration) for selected exposures that follow the symptomatology were used to correlate the visual symptoms with actual metabolic responses to the exposure and both should be considered together in evaluating actual vegetation effects.

Range-Finding Test Series. The HC RFT was conducted with air concentrations between 400 to 500 mg/m^3, which represent an effective concentration for field obscuration. Based on previous deposition velocity data, anticipated foliar mass loading, and anticipated phytotoxicity, exposure times were reduced from the typical 2, 4, 6, and 8 h, employed for phosphorus and fog oil tests, to 1, 2, 3, and 4 h; smoke concentration were 410, 480, 380, and 450 mg/m^3 air, respectively. Exposures were conducted at 2 mph, 40 to 45% RH, and a temperature of 22°C. Mass loading data for this test series are provided in Table 3.31.

The concentration of Zn associated with foliar surfaces ranged from 2 to 16 mg Zn/cm^2 (Table 3.31). In general, contact toxicity responses for the four plant species to the HC smoke included chlorosis (chl), necrotic spotting of leaves (NS), tip burn (TB) in the pine or leaf burn (LB), and leaf drop (LD) in extreme cases (Table 3.35). Overall, damage was marginal compared with the phosphorus and fog oil smokes, although deposited dose for the HC exposures was less. The rapid appearance of chlorosis and subsequent necrotic spotting is probably the result of Zn absorption from foliar surfaces and its subsequent interference with Fe metabolism. This is a common response to excess Zn.

TABLE 3.35. INFLUENCE OF EXPOSURE DURATION (FOLIAR MASS LOADING) ON TOXICITY RESPONSE OF PONDEROSA PINE, SAGEBRUSH, TALL FESCUE, AND BUSHBEAN TO HC SMOKES (RFT)

Plant Species	Exposure Duration (h) 1	2	3	4
	(DR Rating Scale) [a]			
Ponderosa Pine	1,NS,TB,OGA	2, NS,TB	2,TB(0.5-2)	3,TB(0.5-3)
Sagebrush	1,chl,OGA	1,chl	2,LB,LD	2,chl,LB,LD
Tall Fescue	2,NS,chl,OGA	4,NS,chl	5,chl,NS	5, chl,NS,LB
Bushbean	2,NS,chl,LB,OGA	2, NS,chl,O&NGA	5,chl,NS,LB	6, chl,NS,LB

[a] Chlorosis (chl), necrotic spotting of leaves (NS), tip burn (TP), leaf burn (LB), leaf drop (LD), and (OGA) old growth affected.

The intensity of foliar damage (DR scale of 0 to 6, damage ranging from 0-5% to 95-100% damage) was proportional to mass loading (Table 3.31). Although damage ratings as high as 5 and 6 are reported, these relate primarily to the extent of chlorosis and necrotic spotting. In no case is damage severe enough to indicate significant leaf drop or dieback of canopies, as observed in severe cases with phosphorus and fog oil smokes. Ponderosa pine and sagebrush were least susceptible to HC smoke damage, while the grass species and bushbean were more severely impacted in these exposures. This differential susceptibility may have resulted from thinner cuticles and higher rates of foliar absorption for the latter species. With the exception of bush bean, all observed damage was restricted to older needles and/or leaf blades, again supporting the contention that absorbed Zn may be interfering with Fe metabolism, an effect which is generally restricted to older tissues. In bush bean, damage was restricted to older tissues at the lowest mass loading, while both old and younger tissues were affected at exposures in excess of 1h.

Wind Speed Test Series. The following assessments of HC smoke phytotoxicity are based on the assumption that Zn, as soluble $ZnCl_2$, is the primary HC smoke constituent responsible for the observed effects. The organic constituents deposited to foliar surfaces in these studies are presently assumed to be of low enough concentration, and short enough persistence, as not to be implicated in the toxicity responses.

Although the foliar mass loading rates for HC were substantially below those for the other smokes tested, effects appear to be evident. Toxicity symptoms appeared within two days of exposure in the bushbean, but not for 3 to 6 days in the pines, sagebrush, and grass.

Ratings of damage intensity and symptomology at termination of the study, 30 days postexposure, are given in Table 3.36. In general, Daubenmire damage ratings (DR scale) below 2 are not considered as significant, based on the frequency of tip burn and needle or leaf blade dieback observed in control plants. On this basis, tall fescue and bushbean are most susceptible, with damage evident at approximately 5 μg Zn/cm^2. The other plant species exhibit detectable damage at approximately 20 μg Zn/cm^2. The 10-mph treatments, which had the highest foliar mass loading rates, showed the most pronounced damage. This damage was in the form of tip or blade burn, chlorosis, and necrotic spotting. Except for bush bean, these symptoms were confined to the older tissues. In no case was there any apparent damage to buds or expanding leaves.

Postexposure leaching of exposed plants had mixed impacts. At low foliar doses, there appeared to be some amelioration of the intensity of effects; at high loadings (10 mph), effects were intensified in short-needle pine and bush bean, and reduced in sagebrush and tall fescue. This difference in response, following application of a simulated rainfall, can be assumed to result from differences in soluble contaminants associated with foliage, and the rates of removal versus foliar absorption. Overall, the toxicity results obtained for HC exposures are consistent with Zn- and/or acid-induced damage. The tip burn and necrotic spotting are consistent with salt/acidity damage as observed with the phosphorus smokes; while the chlorosis and vein darkening would suggest an interference of Zn with Fe homeostasis. Because Zn and Fe are both essential trace elements, a comparatively low-concentration should elicit the observed effects.

Relative Humidity Test Series. The contact toxicity of HC smokes appears not to be significantly affected by relative humidity (Table 3.37). No consistent trends were noted with any of the five plant species. Overall, sagebrush exhibited the least degree of response to HC smokes in this exposure series, while bush bean was again the most sensitive. Toxicity responses were generally confined to tip burn, necrotic spotting, and some chlorosis. All effects were confined to the older tissues, with new growth appearing normal.

Postexposure leaching resulted in no amelioration or intensification of toxicity responses observed for other smokes. In general, rainout during smoke generation, substantially reduced adverse plant effects in all cases except that for bushbean. All of the noted plant effects are consistent with Zn absorption being responsible for toxicity. As with the wind speed test results, reported mass loading rates for organic constituents of HC smokes, and their lack of persistence, would rule out a significant impact from these components. Further, bushbean toxicity responses included a pronounced "purple veining", consistent with nutrient ion imbalance.

TABLE 3.36. PHYTOTOXICITY OF HC SMOKE COMPONENTS, AND INFLUENCE OF POST EXPOSURE SIMULATED RAINFALL ON TOXICITY (WST)

Plant Species/ Treatment	Foliar Mass Loading (µg Zn/cm^2)	Post Exposure Toxicity Responses[a] Damage Index (DR Scale)	Symptomatology[b]
Ponderosa Pine			
2 mph-exposed	4	1.3	TB
-leached		1	TB
4 mph-exposed	12	1	TB
-leached		1	TB
6 mph-exposed	16	2	TB
-leached		1.5	TB
10 mph-exposed	143	2.3	TB,chl,NS
-leached		2.5	TB,chl,NS
Short-Needle Pine			
2 mph-exposed	6	1	TB, NS
-leached		1	TB
4 mph-exposed	10	1.3	TB,chl,NS
-leached		1	TB,chl,NS
6 mph-exposed	12	2	TB,chl, NS
-leached		1	TB
10 mph-exposed	89	3.6	TB,chl,NS
-leached		4.5	TB,chl,NS
Sagebrush			
2 mph-exposed	6	1	TB
-leached		1	TB
4 mph-exposed	16	1	TB
-leached		1	TB
6 mph-exposed	21	1.6	TB
-leached		1	TB
10 mph-exposed	72	3.3	TB
-leached		1.5	TB
Tall Fescue			
2 mph-exposed	3	1	TB,chl
-leached		1	TB,chl
4 mph-exposed	6	1.3	TB,chl
-leached		1	TB,chl
6 mph-exposed	5	2	TB,chl,NS
-leached		1	TB,chl,NS
10 mph-exposed	10	4.6	TB,chl,NS
-leached		2.5	TB,chl,NS
Bushbean			
2 mph-exposed	4	2	chl, NS
-leached		1.5	chl, NS
4 mph-exposed	7	3.6	chl, NS
-leached		3.5	chl, NS
6 mph-exposed	14	4	LB, chl, NS
-leached		3.5	LB,chl,NS
10 mph-exposed	51	5	LB,chl,NS,O&NGA
-leached			4
LB,chl,NS,O&NGA			

(a) Codes for Daubenmire rating scale listed in Table 2.6.
(b) Effects listed appeared only in the older growth, unless otherwise noted.

TABLE 3.37. CONTACT PHYTOTOXICITY OF HC SMOKE COMPONENTS; INFLUENCE OF RELATIVE HUMIDITY, POST EXPOSURE SIMULATED RAINFALL AND RAINOUT AT 3 WEEKS POST TREATMENT (RHT, HC16 TO HC19)

Plant Species/ Treatment	Foliar Mass Loading ($\mu g\ Zn/cm^2$)	Post Exposure Toxicity Response[a]	
		Damage Index (DR Scale)	Symptomatology[b]
Ponderosa Pine			
20% RH-exposed	11	2	TB
-leached	4	4	TB, NS
55% RH-exposed	18	3	TB
-leached	3	1.5	TB, NS
85% RH-exposed	18	2	TB, NS
-leached	7	5	TB, chl
Rainout	5	1	
Short-Needle Pine			
20% RH-exposed	10	2	TB, chl
-leached	1	4	TB, chl
55% RH-exposed	10	2	TB, NS
-leached	1	1	TB
85% RH-exposed	21	3	TB,chl
-leached	2	2	TB
Rainout	5	1	TB
Sagebrush			
20% RH-exposed	16	1	TB
-leached	7	1.5	TB
55% RH-exposed	15	1	TB
-leached	10	1	TB
85% RH-exposed	18	1	TB
-leached	9	1	TB
Rainout	14	1	TB
Bushbean			
20% RH-exposed	10	3	NS,chl
-leached	3	3.5	[illegible] chl
55% RH-exposed	11	4	NS,chl
-leached	6	3	NS,chl
85% RH-exposed	15	3	NS,chl
-leached	5	3.5	NS,chl
Rainout	10	5	NS,chl,LB,LC
Tall Fescue			
20% RH-exposed	7	3	NS,chl
-leached	0.5	2	NS,chl
55% RH-exposed	10	2	TB,NS
-leached	2	1	NS
85% RH-exposed	12	2	TB,NS
-leached	4	1.5	NS,chl
Rainout	2	1	NS

(a) Codes for Daubenmire rating scale listed in Table 2.6.

(b) Effects listed appeared only in the older growth, unless otherwise noted.

Cumulative Dose Test Series. The response of the vegetation to cumulative doses of the HC smoke was more acute than had been previously observed in such species as bush bean, sagebrush, and short needle pine. The results (Table 3.38) indicate that these three exhibited the greatest response to the smoke, especially at the higher concentrations, and that again most of the apparent damage was confined to the older tissues. In the bush beans, both the low and high concentrations appeared to affect the old and new tissues, but the damage on the new growth was more characteristic of Zn toxicity than the obvious contact damage of the older foliage. This did include the appearance of the purplish color in the veins and the necrotic spotting.

The high-concentration runs, however, proved to be the most phytotoxic to the beans as the first set of three plants to be exposed to the smoke died after just three exposures. This prompted the use of another set of three plants over the last four exposures. This second set also showed severe damage (see Table 3.27) but were able to recover through the setting of new leaves after the completion of the runs. It was apparent that the continued (frequently repeated in time) contact phytotoxicity of the smoke did not permit sufficient time for the recovery of the first set and the continued loss of photosynthetic tissue exceeded their lethal limit.

Similar consequences of the cumulative doses were also evident in the sagebrush and the short-needle pines. These species have a much slower growth rate than that of the bush bean, especially during the winter months when these exposures took place. The cumulative contact phytotoxic effect of several exposures apparently destroyed too much of the photosynthetic tissue for some of the plants to survive. This was particularly evident again in those plants exposed to the high concentrations.

Shortly after the completion of the exposures, the low-concentration short-needle pines underwent bud break, and the new growth did not exhibit any of the damage symptoms observed in the older exposed tissue. The low-concentration sagebrush, however, did not show any new growth even after 30 days post exposure. It must be noted also that the sagebrush, apparently due to the surface morphology of its leaves, accumulated the highest amount of Zn over both the high and low-concentration runs (Table 3.38). There is a possibility that the level of damage seen in the sagebrush may, therefore, be a Zn toxicity response.

The least amount of damage was evident on the ponderosa pines (Table 3.38). These plants were also beginning to undergo bud break just at the start of the exposures, and this new growth continued during the experiment and beyond. The new growth, especially in the low-concentration plants, did not immediately appear to be affected by the smoke, which

TABLE 3.38. CONTACT PHYTOTOXICITY OF HC SMOKE COMPONENTS; INFLUENCE OF CUMULATIVE DOSE (TWO CONCENTRATIONS, NINE EXPOSURES - HC22-30), 72 H (3/2), AND THREE WEEKS (3/24), AFTER FINAL EXPOSURE

Plant Species/ Treatment/ Date	Foliar Mass Loading ($\mu g\ Zn\ cm^2$)	Toxicity Response[a]	
		Damage Index (DR Scale)	Symptomatology
Bush Bean			
Low Concentration			
3/2/87	4.09	5.3	chl,LD,O&NGA
3/24/87		3[b]	chl,TB,NS
High Concentration			
3/2/87	8.21	5.5[c]	chl,LBD,OGA
3/24/87		3.5[b]	chl,NS,LC,O&NGA
Sagebrush			
Low Concentration			
3/2/87	18.2	2	TB(0.5),BD
3/24/87		2.5[d]	TB(0.5),BD
High Concentration			
3/2/87	163.3	6	TB(0.5),BD,NNG
3/24/87		6	D
Short-Needle Pine			
Low Concentration			
3/2/87	15.1	5	TB(7.0)
3/24/87		4[b], [d]	TB(7.0),NGDH
High Concentration			
3/2/87	72.3	6[d]	TB(5.0)
3/24/87		5.5[b]	TB(7.0),NGDH
Ponderosa Pine			
Low Concentration			
3/2/87	13.45	1	
3/24/87		1.5	TB(0.5)
High Concentration			
3/2/87	75.68	3	TB(4.5),OGA
3/24/87		4	TB(8.0),OGA
Tall Fescue			
Low Concentration			
3/2/87	5.65	2	TB(3.0),NS,W
3/24/87		4	TB(15.0),NS,W,OGA
High Concentration			
3/2/87	29.3	4	chl,TB(12.0),NS,OGA
3/24/87		5	chl,TB(12.0+),NS,OGA

(a) Daubenmire Scale and symptomatology definitions given in Table 2.6.
(b) Based on new growth.
(c) Rating on second set of plants as first set were dead after three exposures.
(d) Rating based on two of the three plants: third plant dead.

accounted for the low rating. The high-concentration plants had one of the higher mass loading levels of the species tested in this experiment with an accompanying higher damage index. The increase in damage level after the exposures was evident in the old growth and may also reflect a increasing response to Zn toxicity within these tissues.

The grasses were definitely affected over the course of the experiment, but once again only those tissues that were directly exposed to the smoke were affected. The increase in the damage level over the time following exposure was accounted for by the increase in tip burn in the older tissues. The newer portions at the base of the leaf shoot did not appear to be affected and the rate of growth was not affected (see Section 3.6.5).

As noted previously, in all species only the older tissue was affected by the exposures. Growth emerging after the completion of the exposure series was not usually affected, with the exception of the bush beans, which were also under high amounts of stress from previous leaf loss. Those effects noted were similar to that of foliar absorbed Zn toxicity.

3.6.4 Effects of HC Smoke on Photosynthesis and Respiration

Options for the quantitative assessment of plant damage to augment the nonparametric phytotoxicity data discussed above were considered. Two options were considered; these included use of either polarography or CO_2 gas analysis to quantitate the metabolic effects of obscurant smokes based of rates of photosynthesis and respiration. The former procedure was evaluated as part of the present WST series, while the latter was performed for the cumulative dose test series. Both procedures have experimental shortcomings. Polarographic methods use very small samples of vegetative tissue; thus, results can be nonrepresentative. Gas exchange via infrared analysis of carbon dioxide can employ the entire plant canopy, but lacks a nondestructive means of assessing total biomass evaluated, and thus lacks suitable controls.

Wind Speed Test Series. The polarographic method was used to compare phenotypic plant responses, shown in Table 3.36 for sagebrush, to metabolic effects with time following exposure. This rather fast and inexpensive method permitted evaluation of the rates of oxygen consumption resulting from respiration, and the rates of oxygen production resulting from operation of photosystem II (Hill reaction, PS II). In practice it should provide a basis for assessing the impacts of foliar-absorbed smoke components on electron transport systems associated with these two basic plant processes.

Results for sagebrush are shown in Figure 3.28. In the case of photosynthesis, there appears to be little or no effect of HC smoke contaminants in the 2- and 4-mph treatments; while in the 6 mph treatment (21 μg Zn/cm^2), there is significant depression oxygen evolution at 1 day postexposure, with a recovery to control rates between 8 and 15 days. At the highest mass loading (10 mph), a similar depression and more pronounced increase in oxygen evolution is apparent at 8 days, with recovery to control rates by day 15. Results for respiration are qualitatively similar to photosynthesis, except that it appears to be a more sensitive indicator of smoke effects. This is seen in both the depression and increased oxygen consumption for the 6- and 10-mph treatments.

A comparison of this data set for sagebrush, with that in Table 3.36, indicates that this approach not only correlates dose with impacts but also provides additional information. For example, while the phenotypic data do not indicate a definitive effect for the 6-mph treatment, it is clearly seen in the polarographic data, particularly in the respiration data. In addition, these data show the onset of HC smoke components effects to be present at 1 day rather than 30 days, the maximum effect at approximately 8 days, and a recovery by 15 days postexposure. It is assumed that the effects observed, both with respect to the phenotypic damage and rates of oxygen consumption and evolution, reflect the extent of metabolic disruption, specifically on electron transport systems. While this approach seems to be a more sensitive indicator of smoke damage, we do not feel that it can totally replace the gross damage indices currently employed. This judgment is based on the end use of these smoke data, namely to provide readily usable indices to assess smoke impacts at training installations. Specifically, the metabolic type data say little concerning the extent of damage to specific plant components that influence longer term plant survival, i.e., damage to meristematic tissue, or older and younger growth.

Cumulative Dose Test Series. Measurements of individual plants in the CDT series were taken prior to exposure and at various times during the time couse of exposures from plants in both the high and low-concentration series. Control plants not exposed to HC smoke were also measured intermittently over this period, to provide a point of reference.

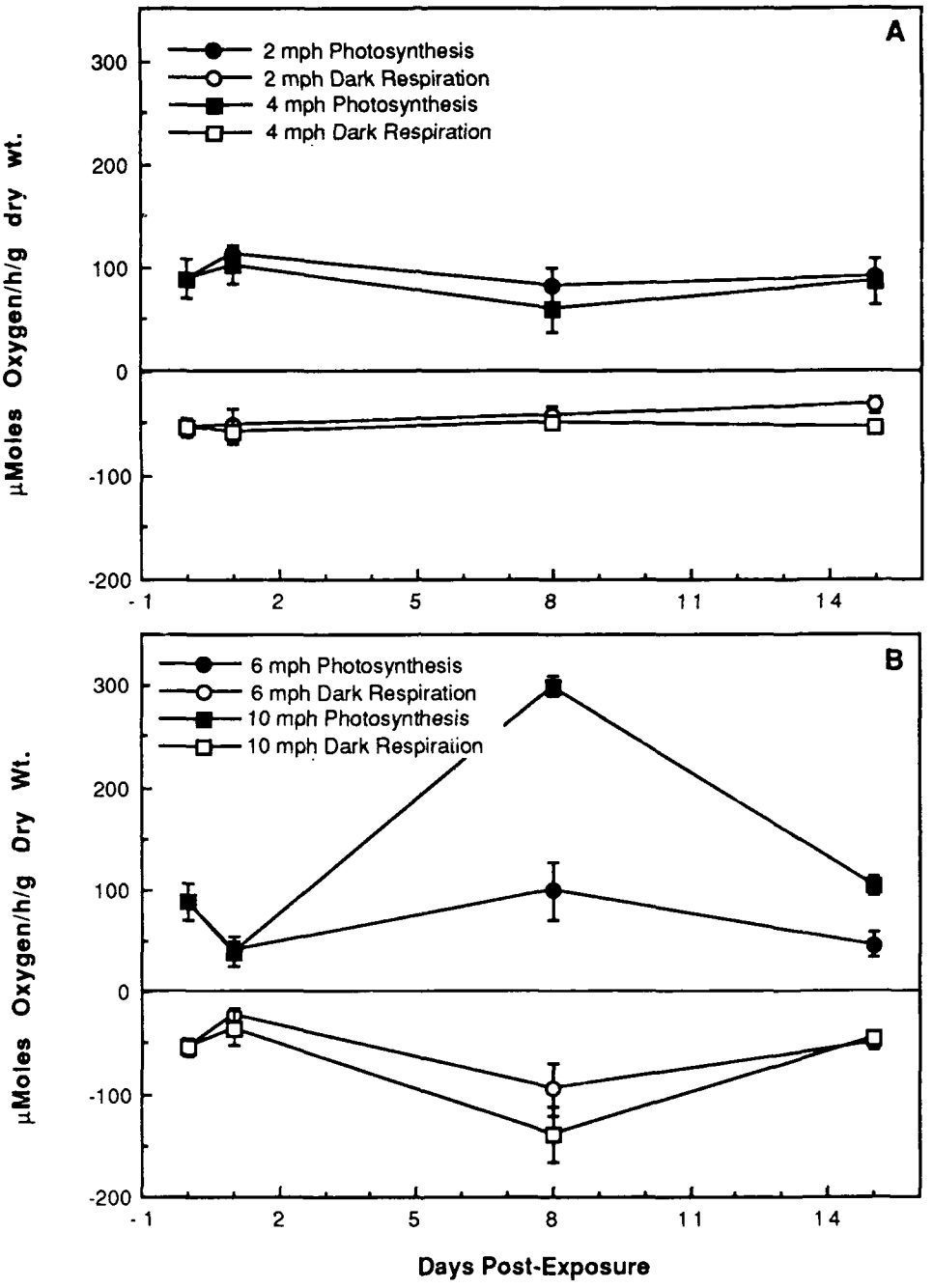


FIGURE 3.28. TIME COURSE OF HC SMOKE DAMAGE TO LEAF TISSUES OF SAGEBRUSH. PHOTOSYTHETIC OXYGEN EVOLUTION AND RESPIRATORY OXYGEN CONSUMPTION MEASURED BY POLAROGRAPHY IN PLANTS EXPOSED TO SMOKES AT WIND SPEEDS OF 2, 4, 6, and 10 MPH

In addition to the continued monitoring of plants exposed to the CDT series and as a means of following recovery from a single exposure, just before to the final exposure day the control plants were measured and then exposed in the final high-concentration run. They were then monitored over the next 2 weeks to determine the potential time course of recovery from adverse HC smoke impacts.

The results of all NCE (net carbon dioxide exchange) measurements taken during the cumulative dose runs are given in Figures 3.29 to 3.33. They are grouped by species to emphasize differences between the low-and high-concentration exposures. Included in each of the figures are the rates from a control plant as a reference. Increases noted in some of these controls were caused by increased leaf area/photosynthetic rates in the faster growing species such as bush bean and tall fescue. Photosynthesis (net CO_2 uptake) is presented as a positive value (net gain in dry weight=growth) and conversely dark respiration is presented as a negative value.

Bush beans exhibited a marked response to the HC exposures both at the low and high concentrations (Figure 3.29, A and B). In the low-concentration plants there was an apparent gradual decline in net photosynthetic capacity compared to the controls over the duration of the experiment (Figure 3.29B). Dark respiration rates remained fairly constant during this time and were very similar to those of the control plants. The HC exposures appeared to have a cumulative effect in the low-concentration bush beans, as phytotoxic symptoms appeared first in the mature leaves and then affected each new leaf as it emerged during the exposure series. The physiological effects of these visible symptoms were initially observed in the carbon fixation (chloroplast-based) processes contributing to a loss of plant photosynthetic ability, but did not appear to immediately affect the mitochondrial CO_2 evolution.

In the high-concentration series, however (Figure 3.29B), there were similar but more immediate and dramatic phytotoxic effects on the foliage with accompanying physiological responses. Net photosynthetic ability was lost within 24 h following the first high concentration exposure (Plant #1). Respiration (CO_2 evolution) was no longer detected within 48 h (24 h after the second exposure). Additional bush beans (Plant #2) were substituted and exposed to the high concentrations later in the series with similar results. Within 24 h after the second exposure the plants exhibited severe phytotoxic symptoms and no apparent photosynthesis.

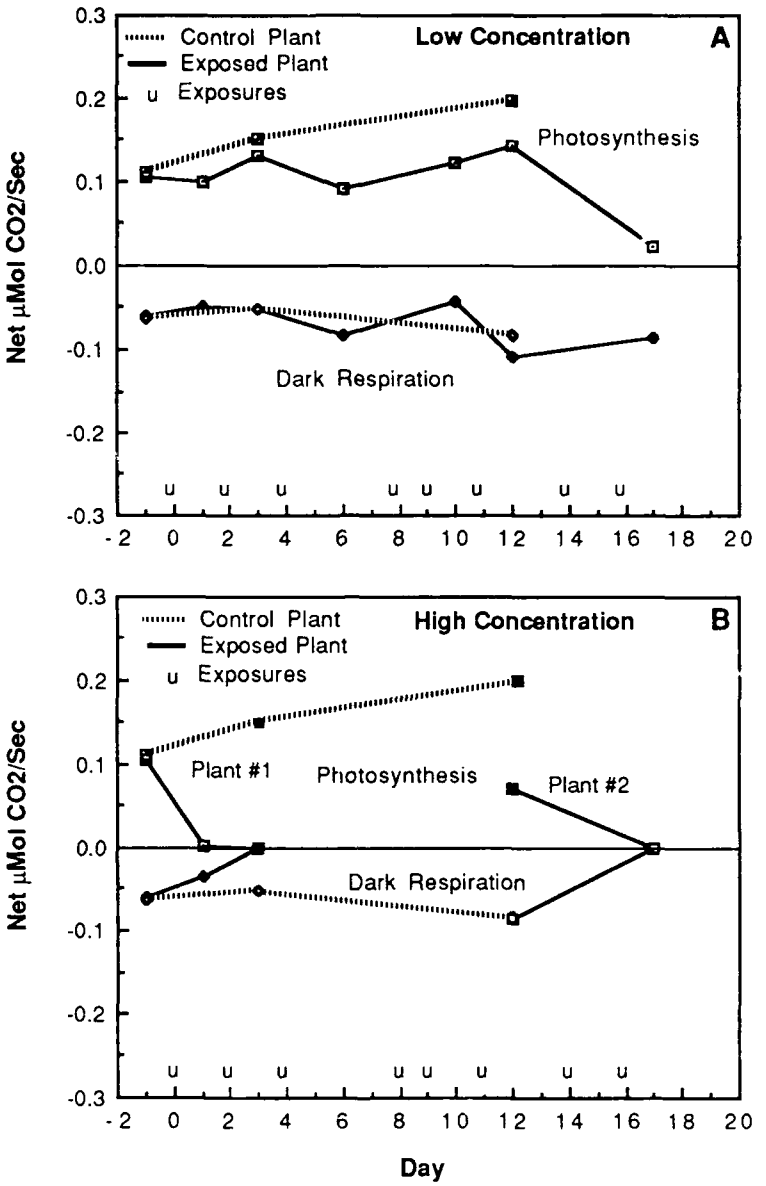


FIGURE 3.29. NET PHOTOSYNTHETIC AND DARK RESPIRATION RATES (Net µmol CO_2 s^{-1}) FOR BUSH BEAN CONTROL PLANT AND EXPERIMENTALS EXPOSED TO LOW-CONCENTRATION (A) AND HIGH-CONCENTRATION (B) CUMULATIVE DOSES OF HC SMOKE OVER A 3-WEEK PERIOD. DATA POINTS FOR THE EXPOSED PLANTS ARE AVERAGES OF TWO PLANTS. TWO SETS OF PLANTS WERE EXPOSED TO THE HIGH CONCENTRATIONS (B). PLANT NUMBER 1 SURVIVED TWO EXPOSURES AND WAS TERMINATED. PLANT NUMBER 2, FIRST EXPOSED AT DAY 14, ALSO SURVIVED TWO EXPOSURES AND WAS TERMINATED

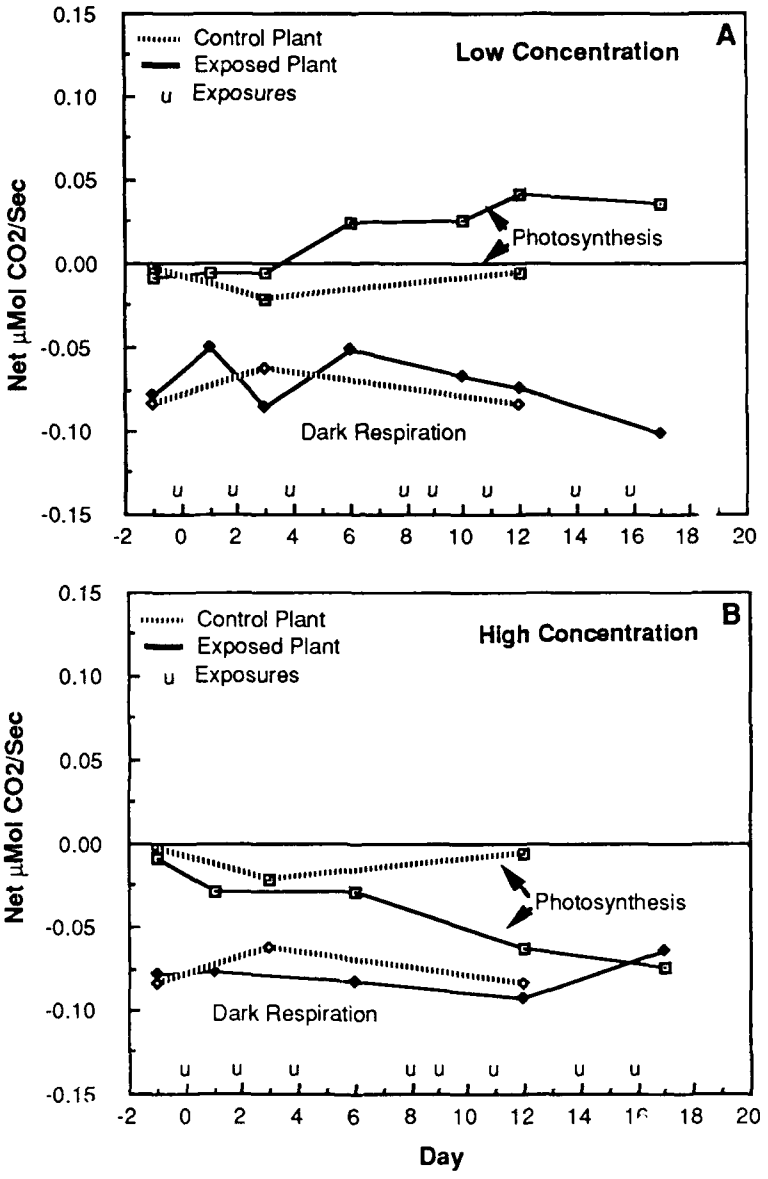


FIGURE 3.30. NET PHOTOSYNTHETIC AND DARK RESPIRATION RATES (Net µmol CO_2 s^{-1}) FOR SAGEBRUSH CONTROL PLANT AND EXPERIMENTALS EXPOSED TO LOW-CONCENTRATION (A) AND HIGH-CONCENTRATION (B) CUMULATIVE DOSES OF HC SMOKE OVER A 3-WEEK PERIOD. DATA POINTS FOR THE EXPOSED PLANTS ARE AVERAGES OF TWO PLANTS

The sagebrush appeared less sensitive to HC smoke at the lower concentrations (Figure 3.30, A and B) than was previously observed in Figure 3.28. Net photosynthetic and respiration rates for the low-concentration plants were higher than those of the controls (Figure 3.30A). All the sagebrush plants used in these experiments were raised in the greenhouse before being acclimated in the growth chambers for the experiment. These experiments were conducted during the winter months when these plants are normally dormant. In this instance the control plants apparently remained in this dormant stage during this period, while the low-concentration plants appeared to have been stimulated to produce new foliage. This response may be attributable to the Zn, that is known to affect the production of auxin at low concentrations.

Those sagebrush plants exposed to the high-concentration levels exhibited no net carbon fixation during the entire exposure series (Figure 3.30B). The higher levels appeared therefore not only to have stopped the carbon fixation capacity, but also to have stimulated the respiration levels in the light while not affecting those in the dark. This may indicate a damage response within the photosynthetic apparatus, and one which is increasing in severity with continued exposure.

The short-needle pines were also originally raised in the greenhouse before to transfer to the growth chamber during January and appeared to be in a dormant stage of growth during much of the experiment. Both the high- and low-concentration plants exhibited no net photosynthetic capacity during their respective exposure series (Figure 3.31, A and B) with a fairly constant level of dark respiration. There were significant phytotoxic symptoms in the high-concentration plants toward the end of the exposure series, however, prompting the termination of two of the three plants. The severity of these symptoms precluded the gas exchange measurements, since it was evident that the plants would not survive.

The ponderosa pine exposed to HC smoke exhibited responses similar to those of the sagebrush for this experiment (Figure 3.32, A and B). The low-concentration plants that initially appeared to be in a dormant condition proceeded to break bud and commence new leaf growth, contributing to the observed increase in net photosynthesis (Figure 3.32A) compared to the control plants which remained in a dormant state.

In the high-concentration series, however (Figure 3.32B), there were similar but more immediate and dramatic phytotoxic effects on the foliage with accompanying physiological responses. High concentrations of the HC appeared to inhibit new growth and completely eliminated net photosynthesis for the duration of the exposure series (Figure 3.32B). Respiration rates were elevated both in the dark and apparently in the light as well. The

responses observed are again potential Zn toxicity, initially, effecting the photosynthetic functions and subsequently those of respiration and general metabolism.

Tall fescue exhibited an initial negative response to smoke exposures at both the low and high-concentration levels (Figure 3.33, A and B). The net photosynthesis of the low-concentration plants appeared to recover rapidly, and, although still not achieving control levels, increased at a steady pace over the remaining exposure series (Figure 3.33A). These increases are most probably attributable to new growth over this period. In the high-concentration plants, although there was an initial recovery of net photosynthetic capability (Figure 3.33B) a subsequent decline was observed. No apparent change was observed in the dark respiration rates over this period. Again there appeared to be a greater sensitivity of the photosynthetic apparatus during this experiment, and the responses were proportional to the amount of actual exposure that the plant received.

Single-Exposure Recovery. Net photosynthetic and dark respiration rates of the control plants for all five species used during the cumulative dose experiments were measured just prior to the final exposure. These plants were then included in the final high-concentration exposure run and subsequently sampled over the next 2 weeks as indicators of recovery patterns from a single exposure. The results of these measurements are given in Figure 3.34 A through E.

Bush bean, the most sensitive to continued high-dose exposures as given previously, also showed initial photosynthetic decline accompanied by phytotoxic symptoms on the older leaf tissue. However, since this was a single exposure, the new growth that quickly emerged over the next few days was unaffected by the contact phytotoxicity of tne smoke and therefore accounted for the subsequent recovery in net photosynthesis that was observed (Figure 3.34A). Dark respiration in this plant appeared to follow a similar pattern although to a lower degree.

The high-concentration exposure appeared to eliminate again any net photosynthesis in the sagebrush while increasing the respiration rate in the light as it had in the cumulative dose experiments (Figure 3.34B). There was no recovery evident in the sagebrush over the measurement period. Given the potential for the leaf surfaces of the sagebrush to accumulate and retain the smoke constituents, it is possible that a sufficiently high enough level was maintained on the plant to continue the inhibition.

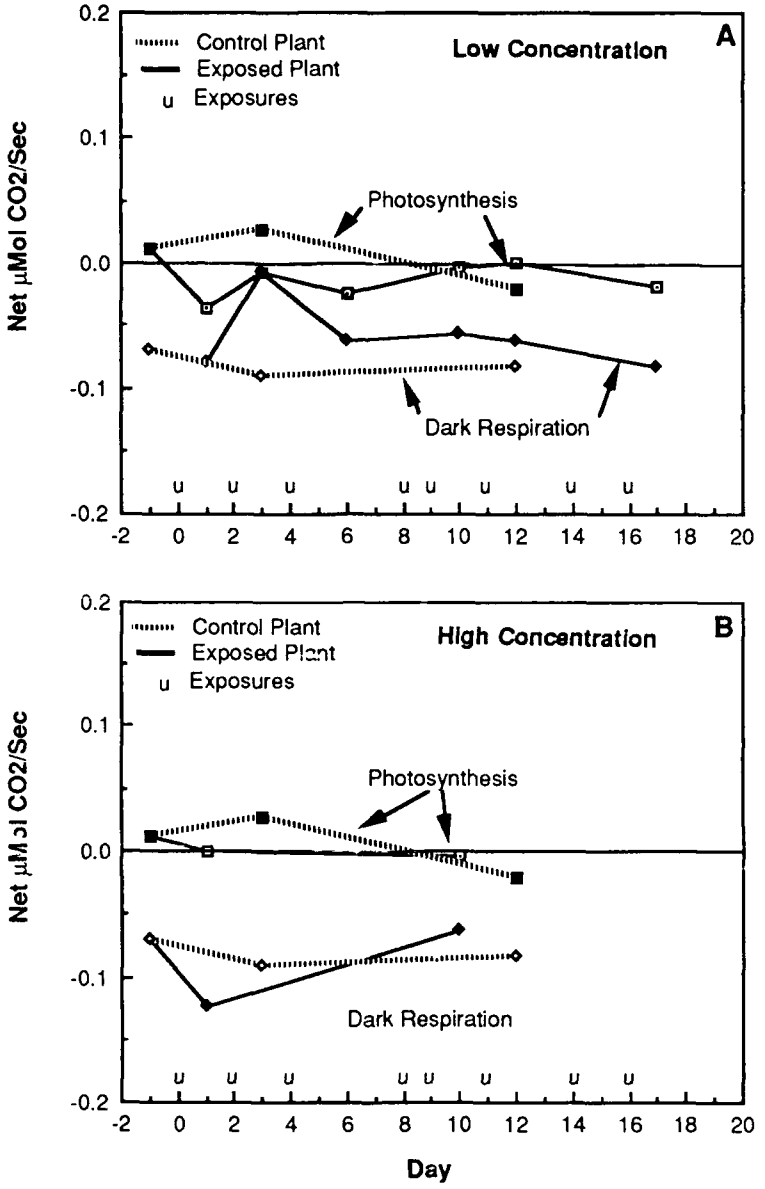


FIGURE 3.31. NET PHOTOSYNTHETIC AND DARK RESPIRATION RATES (Net µmol $C0_2$ s^{-1}) FOR SHORT-NEEDLE PINE CONTROL PLANT AND EXPERIMENTALS EXPOSED TO LOW-CONCENTRATION (A) AND HIGH-CONCENTRATION (B) CUMULATIVE DOSES OF HC SMOKE OVER A 3-WEEK PERIOD. DATA POINTS FOR THE EXPOSED PLANTS ARE AVERAGES OF TWO PLANTS

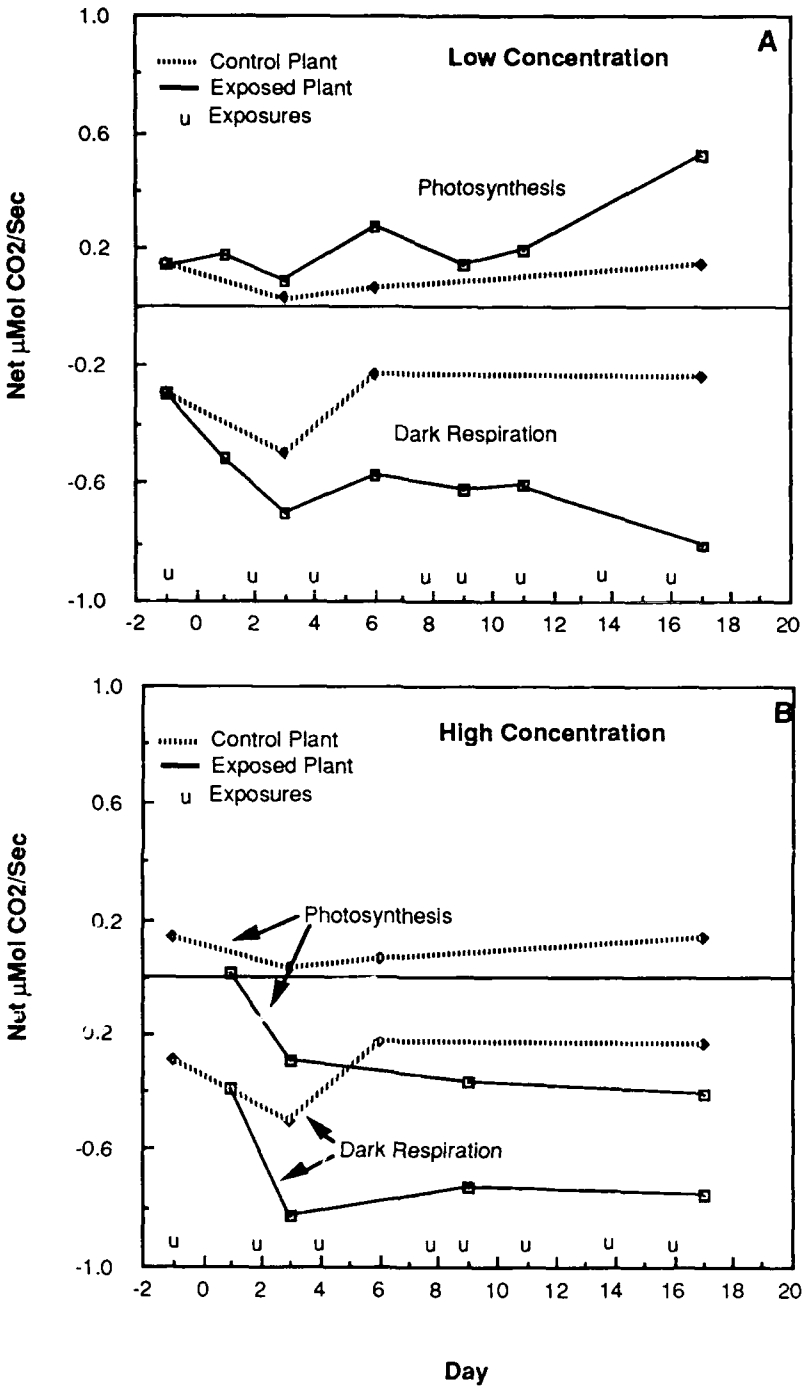


FIGURE 3.32. NET PHOTOSYNTHETIC AND DARK RESPIRATION RATES (Net µmol CO_2 s^{-1}) FOR PONDEROSA PINE CONTROL PLANT AND EXPERIMENTALS EXPOSED TO LOW-CONCENTRATION (A) AND HIGH-CONCENTRATION (B) CUMULATIVE DOSES OF HC SMOKE OVER A 3-WEEK PERIOD. DATA POINTS FOR THE EXPOSED PLANTS ARE AVERAGES OF TWO PLANTS

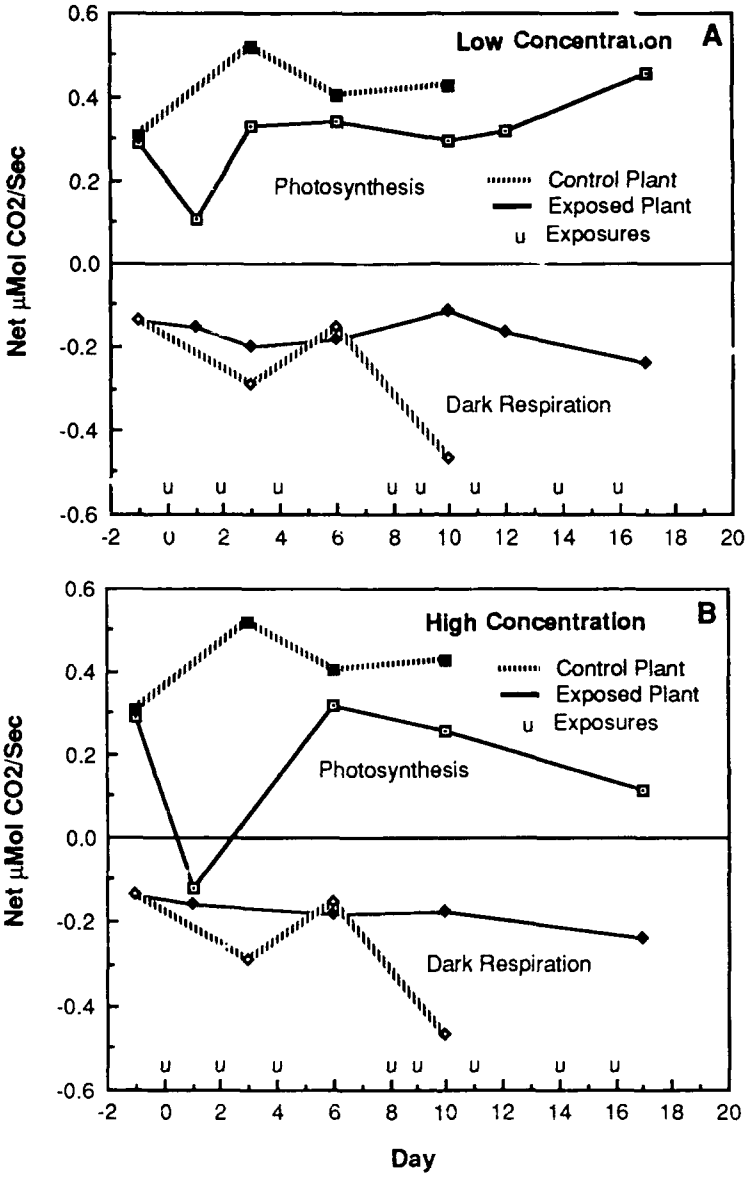


FIGURE 3.33. NET PHOTOSYNTHETIC AND DARK RESPIRATION RATES (Net µmol CO_2 s^{-1}) FOR TALL FESCUE CONTROL PLANT AND EXPERIMENTALS EXPOSED TO LOW-CONCENTRATION (A) AND HIGH-CONCENTRATION (B) CUMULATIVE DOSES OF HC SMOKE OVER A 3-WEEK PERIOD. DATA POINTS FOR THE EXPOSED PLANTS ARE AVERAGES OF TWO PLANTS

The short-needle pine, following a single dose, showed an increase in photosynthetic activity and a decrease in its dark respiration rates over the measurement period (Figure 3.35C). This increase was apparently due to an onset of new growth that had not been exposed to the original smoke.

Following the single high-concentration exposure, the ponderosa pine ceased in the development of new growth and so the initial loss of net photosynthesis and increase in light respiration that was observed was not reversed over the measurement period (Figure 3.35D). Dark respiration remained fairly constant over this period as well.

A similar decrease in rate of new growth development (see Section 3.6.6) may have been responsible for the fairly constant gas exchange rates observed in the tall fescue (Figure 3.34E). Based on the previous growth rates and concomitant increases in net photosynthesis observed in the control tissue before its single exposure, it could be interpreted that this constant rate was, in actuality, an overall inhibition that lasted at least for the 2 weeks when the measurements were taken.

The results of these and previous experiments demonstrate that HC smoke can have a direct adverse effect on the photosynthetic apparatus, both the electron transport (O_2 evolution) and carbon (CO_2) fixation capacity. There does not appear to be a direct effect on mitochondrial respiration evident on the whole plant level unless damage becomes excessive and prolonged. Damage occurs only at those sites actually exposed to the smoke, and foliar morphology can contribute substantially to this accumulation.

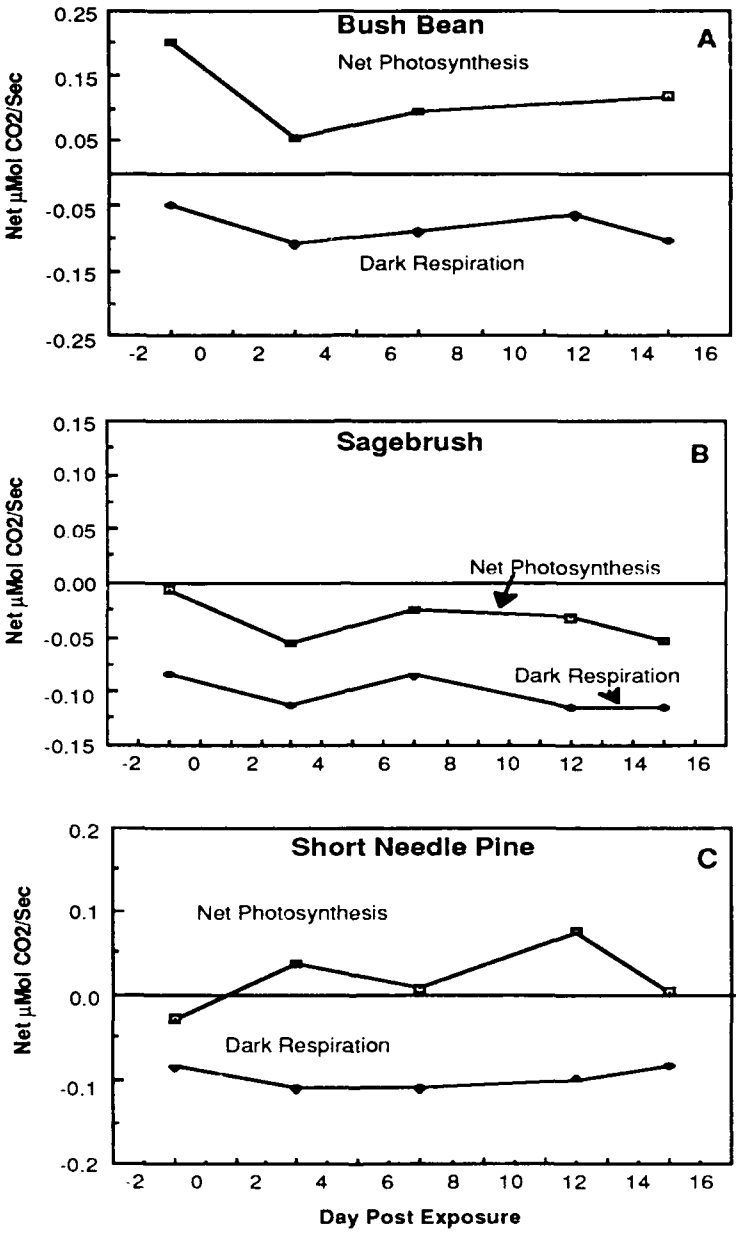


FIGURE 3.34. TIME COURSE OF RECOVERY OF NET PHOTOSYNTHETIC AND DARK RESPIRATION (Net µmol CO_2 s^{-1}) IN INDIVIDUAL PLANTS FOLLOWING A SINGLE HIGH-CONCENTRATION EXPOSURE TO HC SMOKE IN (A) BUSH BEAN; (B) SAGEBRUSH; (C) SHORT-NEEDLE PINE; (D) PONDEROSA PINE; AND (E) TALL FESCUE

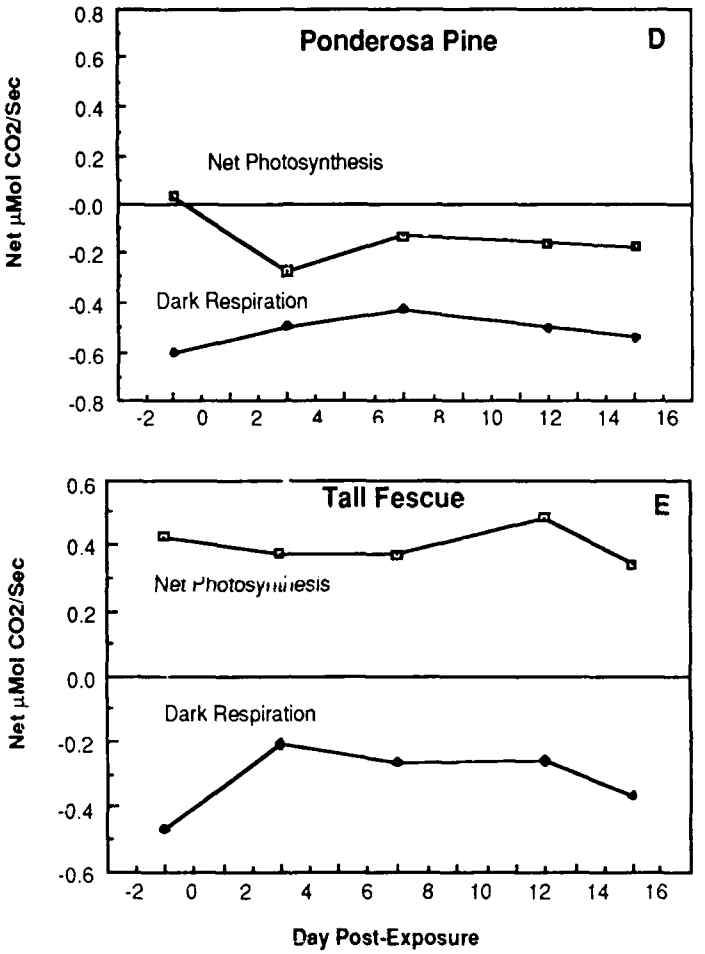


FIGURE 3.34 (Cont). TIME COURSE OF RECOVERY OF NET PHOTOSYNTHETIC AND DARK RESPIRATION (Net µmol $C0_2$ s^{-1}) IN INDIVIDUAL PLANTS FOLLOWING A SINGLE HIGH-CONCENTRATION EXPOSURE TO HC SMOKE IN (A) BUSH BEAN; (B) SAGEBRUSH; (C) SHORT-NEEDLE PINE; (D) PONDEROSA PINE; AND (E) TALL FESCUE

3.6.5 Residual Effects of HC Smoke on Plant Growth

The purpose of the residual effects portion of these studies is to determine whether smoke contaminants are absorbed into the plant following foliar contamination, and, if so, to determine whether there is an impact on plant performance or biomass production through at least two growth cycles. For a residual effect to be apparent, the absorbed contaminant would need to be transported to the root where any adverse effects would be reflected in subsequent regrowth, or dry matter production, in vegetative tissue. This procedure is performed with the grass species since it is the only one of the plants employed with a relatively high growth rate. The grasses that were foliar contaminated with HC smokes in each of the scenarios given previously were harvested 3 weeks postfoliar exposure, cut back, dry matter production determined, and subsequently allowed to regrow for a second or in some cases a third harvest to identify any residual effects of foliar applied smoke on overall growth.

Range-Finding Test Series. The results for the HC RFT are shown in Table 3.39. Based on dry matter production in plants exposed to HC smokes for 1 to 4 h, no significant reductions in dry matter production were observed for either the first harvest of foliar-contaminated grass, or the subsequent regrowth harvest ($P \geq 0.1$). This lack of observable effects would seem reasonable, based on the relatively low Zn mass loadings to foliage of 2.2 to 8.4 $\mu g/cm^2$.

TABLE 3.39. RESIDUAL EFFECTS OF FOLIAR-DEPOSITED HC SMOKE CONTAMINANTS ON DRY MATTER PRODUCTION AND SECOND HARVEST PERFORMANCE OF TALL FESCUE IN RANGE FINDING (RFT) EXPOSURES

Exposure Duration (h)	Dry Matter Production (g dry weight) First Harvest (3 weeks)	Second Harvest (4 weeks)
Control	11.65±0.73	3.93±0.39
1	10.29±0.56[a]	4.01±0.39[a]
2	9.93±0.40[a]	4.35±0.65[a]
3	9.12±0.78[a]	3.92±0.34[a]
4	10.24±0.74[a]	4.11±0.32[a]

(a) Not significant ($P \geq 0.1$) according to two-tailed t-test.

Wind Speed Test Series. The results shown in Table 3.40 indicate that there was no significant residual impact of HC smoke constituents following foliar deposition at higher wind speeds ($P \geq 0.1$) for the first harvest compared to controls for the unleached treatments. This was not surprising based on the relatively low mass loadings. Second harvest results for the exposed plants tend to indicate a residual effect of HC smokes in the unleached treatments at the higher two wind speeds ($P \leq 0.1$).

TABLE 3.40. RESIDUAL EFFECTS OF HC SMOKE CONSTITUENTS ON BIOMASS PRODUCTION IN TALL FESCUE. PLANTS EXPOSED TO HC SMOKES AT 2, 4, 6, AND 10 MPH, AND HELD FOR 21 DAYS, CROPPED, MAINTAINED FOR AN ADDITIONAL 30 DAYS AND SECOND HARVEST BIOMASS DETERMINED

Treatment	Mass Loading ($\mu g\ Zn/cm^2$)	Biomass Production (g dry wt)	
		First Harvest	Second Harvest
Control	0	10.15±1.26	3.16±0.29
2 mph - exposed	3	8.20±0.20[a]	2.57±0.21[a]
- leached		11.23±0.02[b]	2.99±0.23[a]
4 mph - exposed	6	9.92±0.86[a]	2.91±0.27[a]
- leached		10.72±0.96[b]	3.00±0.10[a]
6 mph - exposed	5	8.98±0.51[a]	2.52±0.11[c]
- leached		10.11±1.47[b]	3.03±0.20[c]
10 mph - exposed	10	8.41±1.26[a]	2.47±0.05[c]
- leached		10.95±1.21[b]	3.21±1.17[c]

(a) Not significant ($P \geq 0.1$) according to two-tailed t-test.
(b) Not significant ($P \geq 0.2$) according to two-tailed t-test.
(c) Significant ($P \leq 0.1$) according to two-tailed t-test.

Application of a postexposure simulated rainfall resulted in an overall increase in first harvest biomass at all wind speeds compared to unleached or exposed treatments. Although not significant ($P \geq 0.2$), the trend suggests that HC smokes do affect plant growth. This ameliorating effect was also observed for the second harvest results, and were significant for the 6- and 10-mph treatments ($P \leq 0.1$). From these results it was apparent that constituents of the HC smokes were absorbed through the foliage and adversely impacted biomass production, however the impacts appeared to be short lived and minimal. A similar amelioration effect was previously observed with the phosphorus smokes (Van Voris et al. 1987) but not during the fog oil exposures (Cataldo et al. 1988).

Relative Humidity Test Series. The results shown for tall fescue, in Table 3.41, indicate that dry matter production over the 21-day postexposure period was reduced by foliar absorption of smoke constituents. First harvest dry matter production was reduced at each relative humidity and the rainout treatments ($P \leq 0.1$). There is also some indication that postexposure simulated rainfall intensifies the effect perhaps by solubilizing the material on the leaves thereby increasing penetration and reduction in dry weight of these plants. Second harvest results indicate this adverse residual effect is transient, and dry matter production for all treatments are comparable to controls.

TABLE 3.41. RESIDUAL EFFECTS OF HC SMOKE CONSTITUENTS ON BIOMASS PRODUCTION IN TALL FESCUE. PLANTS EXPOSED TO HC SMOKES AT 20%, 55% and 85% RH, RAINOUT, AND POST-EXPOSURE SIMULATED RAINFALL. FIRST HARVEST RESULTS ARE FOR PLANTS 21 DAY POST-TREATMENT, HARVESTED AND ALLOWED TO REGROW FOR AN ADDITIONAL 21 DAYS

Treatment	Biomass Production (g dry wt)	
	First Harvest	Second Harvest
Control	9.74±0.24	2.53±0.24
20% RH-exposed	7.87±0.38[a]	2.24±0.03[b]
-leached	6 93±0.03[a]	2.36±0.10[b]
55% RH-exposed	7.60±0.83[a]	2.42±0.06[b]
-leached	7.76±0.06[a]	2.53±0.20[b]
85% RH-exposed	8.87±0.65[a]	2.43±0.34[b]
-leached	7.28±0.87[a]	2.20±0.15[b]
Raincut	7.47±0.11[a]	2.40±0.18[b]

(a) Significant ($P \leq 0.1$) according to two-tailed t-test.
(b) Not significant ($P \geq 0.1$) according to two-tailed t-test.

Cumulative Dose Test Series. The results for tall fescue, shown in Table 3.42, indicate that there is a significant ($P \geq 0.01$) effect on first harvest biomass production following cumulative exposures to HC smoke, particularly for the high dose treatment. Second harvest results, however, indicate that this residual effect is transient and that the dry matter production by the plants from both concentration series is not statistically significant from the controls.

TABLE 3.42. DIRECT EFFECTS OF CUMULATIVE HC EXPOSURE ON DRY MATTER PRODUCTION IN TALL FESCUE

Harvest Number (days after exposure)	Control	Low Concentration	High Concentration
First (27 days)	10.43±0.33[a]	8.82±1.14	7.05±0.56[b]
Second (57 days)	7.78±0.52	7.64±0.56	7.51±0.45

(a) Average g dry weight ± S.D., N=3.
(b) Significant at 0.01 level according to two-tailed t-test.

3.6.6 Indirect Effects of HC Smoke on Plant Growth

In the indirect effects studies, smoke-contaminated soils (400-g pots) are planted 1 day post exposure with tall fescue to determine whether smoke components deposited in soil can adversely affect plant performance. In the present study, this involves evaluation of germination and dry matter production. The scope of these indirect impacts are expanded to include smoke effects on solubilization of endogenous elements in soils and availability to plants in the wind speed and cumulative dose tests, where larger mass loadings are employed.

Range Finding Test Series. Mass loading rates to soils exposed to HC smokes for 1 to 4 h in the RFT were provided in Table 3.31. Zinc deposited to Burbank soils (0.4 to 2.3 $\mu g/cm^2$) was substantially less than that for Maxey Flats soil (10 to 20 $\mu g/cm^2$). Again, these values arer affected by Zn extractability (see Figure 3.19). The indirect effects of HC smokes, deposited to soil, on dry matter production are provided in Table 3.43. If one assumes that Zn is the major impacting component of the HC smokes, then it is unlikely that any adverse impact would be expected at these loading levels. This conclusion is supported by the results of both the first and second harvest. Biomass production for fescue grown on either Burbank or Maxey Flats soil contaminated with HC smoke exhibited no significant differences from that of the controls. No effect was also noted on germination (95±7%), and plants exhibited no visible Zn/Fe toxicity symptoms such as chlorosis. While this apparent lack of Zn toxicity may be expected from the soil mass loading rates, which ranged to a high of only #20 μg Zn/cm^2 for the Maxey Flats soil, it may also indicate that the organic constituents of HC smokes deposited on the soil surface at the same time either are not accumulated, or are not particularly toxic.

TABLE 3.43. INDIRECT EFFECTS OF SOIL-DEPOSITED HC SMOKES ON GROWTH OF TALL FESCUE IN BURBANK AND MAXEY FLATS SOILS WITH INCREASING EXPOSURE TIME (RFT)

Soil	Exposure Duration (h)	Mass Loading (μg Zn/cm^2)	Dry Matter Production (g dry wt ± S.D., N=3) First Harvest[a]	Second Harvest[b]
Burbank	Control		4.11±0.15	6.69±0.10
	1	0.38	4.68±0.42[c]	7.20±0.61[c]
	2	0.43	4.67±0.10[c]	7.25±0.35[c]
	3	0.98	4.27±0.50[c]	7.07±0.83[c]
	4	2.26	4.48±0.25[c]	7.93±0.55[c]
Maxey Flats	Control		2.98±0.40[c]	5.55±0.37
	1	9.78	3.48±0.21[c]	6.54±0.82[c]
	2	10.56	3.70±0.10[c]	6.16±0.06[c]
	3	16.24	3.36±0.36[c]	6.64±0.31[c]
	4	20.12	3.54±0.28[c]	5.83±0.15[c]

(a) 27 days postexposure.
(b) 90 days postexposure.
(c) Not significant (P≥0.1) according to two-tailed t-test.

Wind Speed Test Series. Wind speed tests were conducted at 2 to 10 mph; air concentration was ~300 μg HC smoke/m^3 (or ~90 μg Zn/m^3), exposure duration was 2 h, and RH was maintained at approximately 60%. Measured mass loading rates of Zn to Burbank soil increased from 1.6 to 6.6 μg Zn/cm^2 soil surface as wind speed was increased from 2 to 10 mph; mass loading rates for Maxey Flats soil increased from 7.5 to 13.7 μg Zn/cm^2.

As in the range-finding tests, no adverse effects on germination were evident (99±4%). Dry matter production results provided in Table 3.44 indicate that HC smokes deposited to soils, at these relatively low dose levels, had no apparent impact on growth of the fescue. These results were not unexpected at these low deposition rates, since soil sorption can significantly reduce these levels of soluble Zn available to the plant for uptake.

TABLE 3.44. INDIRECT EFFECTS OF HC SMOKES DEPOSITED TO SOILS IN THE WIND SPEED TEST SERIES ON GROWTH OF TALL FESCUE

Soil	Treatment	Mass Loading ($\mu g\ Zn/cm^2$)	Dry Matter Production (g dry wt ± S.D., N=3) First Harvest[a]	Second Harvest[b]
Burbank				
	Control		6.30±0.37	9.54±0.62
	2 mph	1.63	6.16±0.24[c]	9.67±0.64[c]
	4 mph	3.86	6.40±0.15[c]	9.70±0.58[c]
	6 mph	4.75	6.64±0.38[c]	10.05±0.18[c]
	10 mph	6.60	6.28±0.34[c]	9.19±1.03[c]
Maxey Flats				
	Control		3.92±0.38	7.89±0.83
	2 mph	7.55	4.04±0.14[c]	6.89±0.60[c]
	4 mph	6.2	4.71±0.26[c]	7.88±0.86[c]
	6 mph	8.90	4.52±0.16[c]	8.18±0.53[c]
	10 mph	13.70	4.40±0.38[c]	7.69±0.81[c]

(a) 60 days post exposure.
(b) 120 days post exposure.
(c) Not significant (P≥0.1) according to two-tailed t-test.

TABLE 3.45. INDIRECT EFFECTS OF HC SMOKES DEPOSITED TO SOILS IN THE RELATIVE HUMIDITY TEST SERIES ON GROWTH OF TALL FESCUE

Soil Treatment Harvest[c]	Mass Loading ($\mu g\ Zn/cm^2$)	Dry Matter Production (g dry wt ± S.D., N=3) First Harvest[a]	Second Harvest[b]	Third[c]
Burbank				
Control		5.62±0.11	10.85±0.29	4.50±0.69
20% RH	8.14	5.79±0.23[d]	10.33±0.72[d]	4.49±0.23[d]
55% RH	7.76	5.54±0.28[d]	10.26±0.64[d]	4.60±0.62[d]
85% RH	9.01	5.58±0.20[d]	10.35±0.37[d]	4.37±0.14[d]
Maxey Flats				
Control		3.28±0.16[d]	8.8±1.02	5.43±0.03
20% RH	10.73	3.08±0.46[d]	9.94±0.23[d]	4.59±0.26[d]
55% RH	10.70	2.81±0.15[d]	8.05±0.31[d]	4.93±0.30[d]
85% RH	21.24	3.15±0.14 [d]	7.98±0.19[d]	5.05±0.46[d]

(a) 60 days post exposure.
(b) 120 days post exposure.
(c) 180 days post exposure.
(d) Not significant (P≥0.1) according to two-tailed t-test.

Relative Humidity Test Series. As in the previous experiments there were no evident effects of the HC smokes on the germination rate of the grass seeds (100±6%). Dry matter production results are provided in Table 3.45. These data indicate again that there was no significant effect of the HC smokes on the subsequent growth of tall fescue when deposited upon the soil surface in these concentrations and that the conditions at the time of deposition do not seem to be affecting the results.

Cumulative Dose Test Series. The purpose of this test was to assess the cumulative impact of recurrent smoke use on soils and performance of plants grown on these soils. This test series normally provides the highest soil mass loading levels for evaluation. The results, provided in Table 3.46, are for the three harvests of tall fescue grown on soils that had been contaminated in the CDT series. Assuming that the lack of impacts on plant biomass production in the previous test series were attributable to low soil doses of materiel, then the CDT series provides the only exposure scenario in which the effect of higher soil doses can be evaluated for indirect plant effects. Results from this test series are shown in Table 3.46. Mass loading of HC smoke ranged from 15 to 167 μg Zn/cm^2 soil for the high-and low-dose treatments, respectively, following nine consecutive exposures. This is equivalent to 60 to 668 μg HC smoke/cm^2 soil. From the harvest data presented there is no significant impact of HC smoke on grass growth ($P \geq 0.2$). These results, based on the high mass loadings, would indicate that the slightly significant trend observed in the indirect effects data for RFT, RHT, and WST series were the result of random variability.

TABLE 3.46. INDIRECT EFFECTS OF HC SMOKE COMPONENTS ON GROWTH OF TALL FESCUE IN CUMULATIVE DOSE EXPOSED BURBANK AND MAXEY FLATS SOILS

Soil Type/ Exposure Level	Mass Loading ($\mu g\ Zn/cm^2$)	Biomass Production (g dry wt ± S.D., N=3) First Harvest[a]	Second Harvest	Third Harvest
Burbank				
Control	0.0	7.78±0.52	15.19±2.64	4.47±0.20
Low Dose	15.4	7.64±0.56[b]	16.09±1.66[b]	4.43±0.26[b]
High Dose	118.2	7.51±0.45[b]	16.22±1.47[b]	4.64±0.39[b]
Maxey Flats				
Control	0.0	5.52±0.26	14.40±1.70	4.42±0.49
Low Dose	26.4	6.03±0.32[b]	15.87±0.26[b]	4.11±0.34[b]
High Dose	167.9	6.44±0.04[b]	16.38±2.31[b]	3.67±0.58[b]

(a) First Harvest 30 days after last exposure; second harvest 90 days after last exposure; third harvest 120 days after last exposure.
(b) Not significant ($P \geq 0.1$) according to two-tailed t-test.

Elemental Composition of Plant Tissues. Although there is an overall lack of indirect effects of soil-deposited HC smokes on biomass production, elemental analyses of tissues were performed to assess the possible impacts of high soil Zn concentrations on overall plant mineral nutrition.

Synergistic or antagonistic interactions of ions in the soils may have additive or more subtle effects on the plants, thus affecting mineral status. To properly assess this, dried tissue from all three harvests of the high-concentration cumulative dose exposures from both soil types were digested and analyzed for the relative content of several plant macro- and microelements. Tissue concentrations of these ions for two harvests are given in Table 3.47.

As expected tissue concentrations of Zn were significantly elevated in all experimental plants grown in either soil although the uptake in tissues from the Maxey Flat soil was much greater, particularly in the high-concentration series. This conclusively shows that the element was available to the plant in the soil solutions and was capable of being accumulated and translocated from the roots to shoots of the plant.

TABLE 3.47. TISSUE CONCENTRATIONS (µg/g dry wt) OF SELECTED ELEMENTS IN TALL FESCUE LEAF TISSUE GROWN THROUGH TWO HARVESTS IN BURBANK AND MAXEY FLAT SOILS EXPOSED TO LOW AND HIGH CUMULATIVE DOSE EXPOSURES [a]

Element	Soil Type Dosage	Tissue Concentration (Avg µg/g dry wt.± S.D., N=3) First Harvest	Second Harvet	ThirdHarvest
Al	Burbank			
	Low	564±29	586±21	446±8
	High	527±44	612±22	424±51
	Control	519±56	559±28	438±12
	Maxey Flat			
	Low	699±19	673±48	696±6
	High	755±53	733±16	685±11
	Control	783±71	699±19	666±74
Ca	Burbank			
	Low	4982±1181	2400±360	2370±139
	High	4682±328	2478±143	2556±87
	Control	5539±388	2946±572	2898±423
	Maxey Flat			
	Low	3740±339	2985±133	2375±178
	High	3930±504	3177±186	2619±119
	Control	3571±454	3123±563	2209±73
Cu	Burbank			
	Low	10±2	3±2	5±2
	High	11±1	4±1	4±1
	Control	9±1	4±1	4±1
	Maxey Flat			
	Low	3±1	2±1	3±1
	High	3±1	3±1	3±1
	Control	3±1	2±1	2±1
Fe	Burbank			
	Low	40±18	7±4	6±1
	High	35±5	6±1	6±1
	Control	28±11	6±1	5±1
	Maxey Flat			
	Low	10±1	4±3	7±1
	High	5±1	4±1	8±1
	Control	13±7	8±3	8±1
K	Burbank			
	Low	25657±4566	11975±2047	17628±1028
	High	27079±1628	11864±864	20556±830
	Control	24279±1497	12362±412	18448±1665
	Maxey Flat			
	Low	21103±1136	7140±372	13136±1646
	High	22490±2269	7294±142	14967±1431
	Control	28366±1275	9529±1353	11234±1484

TABLE 3.47 (Cont)

Element	Soil Type/ Dosage	Tissue Concentration (Avg µg/g dry wt.± S.D., N=3) First Harvest	Second Harvest	Third Harvest
Mg	Burbank			
	Low	3077±643	2402±232	2218±99
	High	2838±71	2462±327	2241±119
	Control	2917±295	2635±266	2331±80
	Maxey Flat			
	Low	1505±145	1023±77	831±113
	High	1435±121	954±63	749±45
	Control	1447±94	1143±132	887±82
Mn	Burbank			
	Low	119±25	64±19	157±4
	High	140±1	65±19	175±8
	Control	97±15	70±12	161±45
	Maxey Flat			
	Low	216±19	59±13	251±15
	High	236±57	85±7	265±28
	Control	288±46	104±36	254±19
P	Burbank			
	Low	5477±1348	2557±548	2935±31
	High	5887±214	2986±372	3108±85
	Control	5103±246	2443±189	3008±147
	Maxey Flat			
	Low	1548±177	2080±178	4264±420
	High	1544±50	2123±192	4508±235
	Control	1783±154	2312±237	3842±138
Zn	Burbank			
	Low	59±21(b)	24±5(b)	21±2(b)
	High	138±21(b)	71±4(b)	57±7(b)
	Control	21±4	13±1	13±1
	Maxey Flat			
	Low	96±16(b)	59±9(b)	52±5(b)
	High	337±36(b)	259±20(b)	221±55(b)
	Control	38±5	36±14	27±3

(a) Soil mass loading (µg Zn/cm^2): Burbank Low-15.4, High-117.7; Maxey Flat Low-23.3, High-167.9. Harvested at 30 (1st), 90 (2nd), and 120 (3rd) days after final exposure.
(b) Significant (P≥0.05) according to two-tailed t-test.

There appeared to be little impact of HC smoke contamination in soils on the elemental composition of tall fescue leaf tissue. The tissue concentrations of Ca, Cu, Fe, K, and Mg for the treatments were not significantly different from the unfumigated controls for any of the three harvests. Similarly, Al was not observed to increase in tissues with dose, even though it is in significant concentrations in the smokes. In addition, no soil differences were noted with respect to tissue concentrations for these elements. Zinc was seen to significantly increase ($P \leq 0.05$) in tissues from 21 µg/g dry wt in control tissues to 59 and 138 µg/g for plants grown on Burbank soil exposed to either the low or high dose of HC smoke. For Maxey Flats soil, control tissue concentrations for Zn were 38 µg/g, compared to 96 and 337 µg/g for the low- and high-dose treatments ($P \leq 0.05$), respectively. It should be noted that although the Zn present in HC smokes is plant available, there appears to be little synergistic effect on either the availability or tissue levels of other ions. This is particularly interesting because Fe transport is thought to be facilitated in the presence of Zn (Foy et al. 1978).

3.7 SOIL MICROBIAL EFFECTS OF HC SMOKES

The effect of obscurant smoke hexachloroethane (HC) on soil microbial populations and soil microbially mediated processes was evaluated. Soil microbial populations in soil play a key role in nutrient cycling and the biodegradation of organic compounds. The decomposition of organic material in soil into mineral forms and the cycling of plant nutrients is mediated by the soil microbial processes.

The decomposition of organic matter by the soil microbial population is critical to the cycling of important nutritional elements (nitrogen, phosphorus, sulfur, and some trace metals). Soil microbial decomposition processes also detoxify xenobiotic chemicals that may be released to the environment. Therefore, any physical or chemical perturbation on the soil system that disrupts these microbially mediated processes can indirectly influence plant growth, and directly affect the soil's ability to decompose organic matter and detoxify xenobiotics.

Soil enzyme activity and respiration of soil are indicative of the activity of the cumulative heterotrophic microbial population. Soil respiration is one of the most frequently used indexes of microbial activity in soil (Anderson 1982). Soil dehydrogenase activity has been used in the past to measure the activity of the soil microbial population and is an index of endogenous soil microbial activity (Moore and Russell 1972). Dehydrogenase enzymes are intracellular and are involved in microbial respiratory processes necessary for the breakdown of organic compounds in soil.

Phosphatases, which can exist extracellularly, are a broad group of enzymes that cleave both esters and anhydrides of phosphates from complex organophosphates. Their activities in the soil are important for the mineralization of phosphorus from soil organic matter (Ramirez-Martinez 1968). Therefore soil phosphatase activity was chosen as an assay to study the effect of HC smoke on phosphorus cycling in soil.

Nitrogen is the nutrient most limiting in agricultural (Stevenson 1982) and arid land ecosystems (West and Skujins 1978). Nitrogen is considered a macronutrient because plants require large quantities of this element for growth. Nitrogen is also an essential element for the soil microbial population. The conversion of organic nitrogen to available inorganic forms combines two distinct microbiological processes: ammonification, which converts organic nitrogen to ammonia; and nitrification, which transforms ammonia to nitrate. Nitrification in soil is mediated by nitrifying bacteria, or nitrifiers. The *Nitrosomonas* spp. are most responsible for the conversion of ammonia to nitrite and the *Nitrobacter* spp. for the further oxidization of nitrite to nitrate, a soluble and mobile form in soil utilizable by plant and other microorganisms.

Soil organisms are also sources of food for the soil fauna (e.g., mites, arthropods, worms) and thus occupy an important position low in the food chain. A deleterious impact on the various soil microbial populations can affect soil invertebrate life and the soil-dwelling animals that depend on the populations for food. Effects of HC smokes on the soil microbial community therefore were evaluated with these four principal soil microbiological parameters, namely, soil respiration, soil dehydrogenase and phosphatase enzyme activities, and soil-nitrifying bacteria populations.

Soil Respiration. Respiration of soil measured by carbon dioxide evolution or oxygen consumption, or both is routinely used for assessing toxicity to aerobic bacteria. It is indicative of the activity of the cumulative heterotrophic microbial population. Heterotrophic activity is responsible for the decomposition of natural and xenobiotic carbon compounds in soils as well as for the cycling and mineralization of essential inorganic nutrients such as nitrogen, phosphorous and sulfur.

Respiration of Palouse soil exposed to HC smoke for 4 h (HC-5) started to show inhibition after 24 h incubation and declined by ~35% after 20 days when compared to the unexposed control (Figure 3.35). Similar effects were observed with Palouse soil exposed to HC smoke at 20 or 85% RH as shown in Figure 3.36. In the cumulative dose exposure experiment, respiration of Palouse soil was not affected initially and up to 90 h but was inhibited by ~45% after 2 weeks incubation when compared to the unexposed control (see Figure 3.37). This indicates that HC smoke inhibits heterotrophic microbial activity. An unexposed control soil amended with 150 mg glucose was included to assure that a viable

heterotrophic population was present as evidenced by the substantial increase in oxygen consumption (see Figures 3.36 to 3.38).

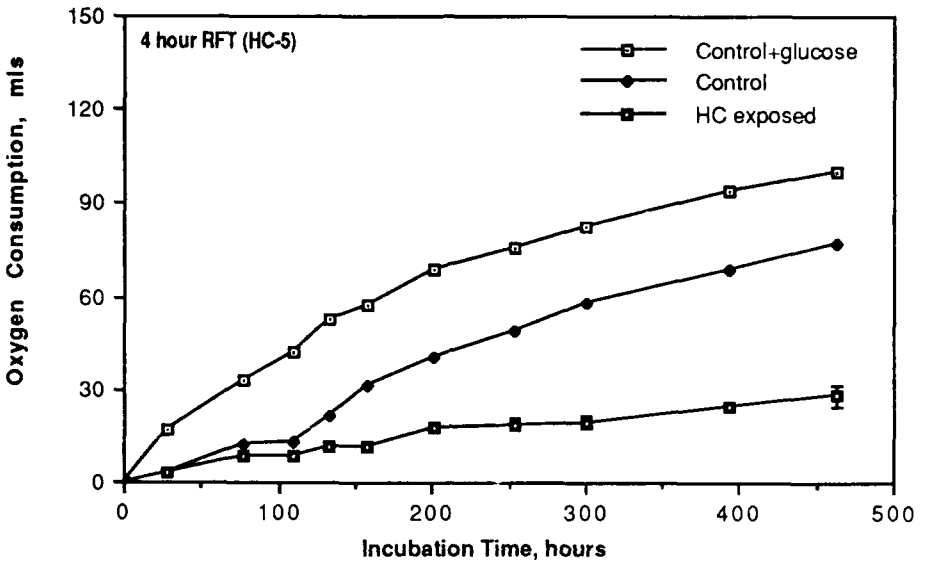


FIGURE 3.35. EFFECT OF 4-H HC EXPOSURE (RFT,HC-5) ON PALOUSE SOIL RESPIRATION. ERROR BARS REPRESENT STANDARD DEVIATIONS, N=2 FOR THE HC EXPOSED CURVE; SINGLE VALUES FOR THE OTHER TWO CURVES

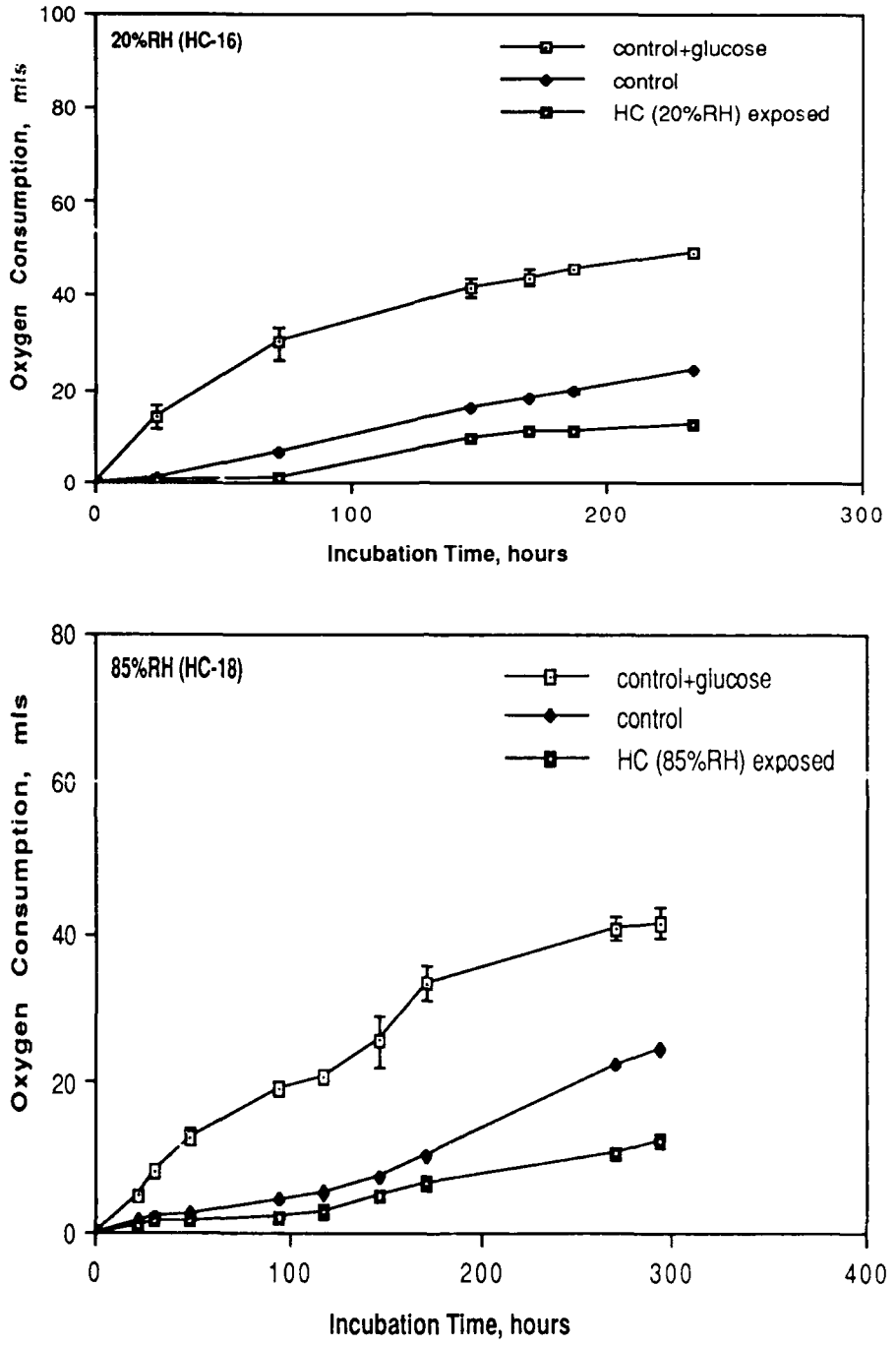


FIGURE 3.36. EFFECT OF HC EXPOSURES (20 AND 85% RH) ON PALOUSE SOIL RESPIRATION. ERROR BARS REPRESENT STANDARD DEVIATIONS, N=2

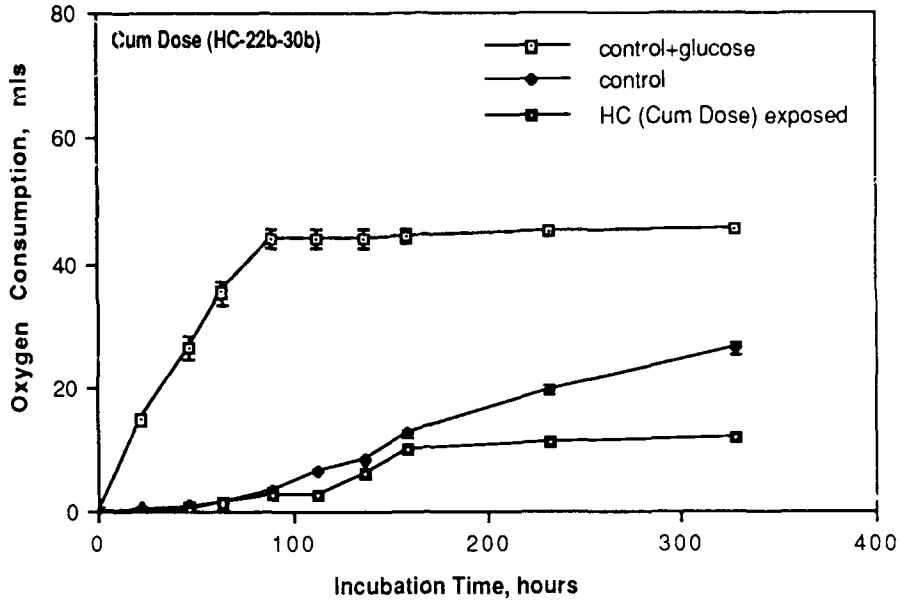


FIGURE 3.37. EFFECT OF CUMULATIVE HC EXPOSURES ON PALOUSE SOIL RESPIRATION. ERROR BARS REPRESENT STANDARD DEVIATIONS, N=2

Soil Dehydrogenase Activity. The inhibition of enzymes that drive key metabolic reactions in microbial cells is likely the underlying cause of chemical toxicity. Microbial dehydrogenase enzyme systems catalyze the oxidation of organic material and fulfill an important role in the soil carbon cycle. The assay of soil dehydrogenase activity is a general indicator of the potential activity of the soil microbial population and has been recommended as an index of general soil microbial activity (Casida 1967; Skujins 1967). This assay was chosen for the HC aerosol effect study because it measures the potential ability of a microbial community to decompose organic matter and to mineralize carbon source to carbon dioxide. Dehydrogenase assay was carried out using glucose as the substrate to study the effects on carbon mineralization. Casamino acids which are high in nitrogen and carbon contents was also employed as a substrate to examine the effect of HC on the mineralization of both nitrogen and carbon combined.

For the range-finding test series, dehydrogenase enzyme activity was measured immediately after each HC exposure (Table 3.48). Figure 3.38 shows that a 1-h exposure of HC in the Burbank soil had a stimulatory effect on dehydrogenase activity for both substrates (glucose and casamino acids) tested. However, the activity declined with increasing exposure time. The 4-h HC exposure caused the enzyme level to decreaseto 27% in soil amended with glucose and to 42% in soil amended with casamino acids.

On the contrary, the effect was very little in Palouse soil. A 4-h HC exposure caused no effect when glucose was used as substrate while the activity was decreased only ~12% in the casamino acids-amended Palouse soil.

Table 3.49 and Figure 3.39 showed the effect of HC on soil dehydrogenase activity based on relative humidity. Inhibition was very severe on Burbank soil amended with either glucose or casamino acids. It ranged from 20 to 55% of unexposed control. In Palouse soil amended with glucose, the activity was slightly inhibited (82 to 96% of unexposed control); however, it recovered and was enhanced with incubation time. After 1 to 2 weeks, the enzyme level increased to 125-169% of unexposed control. In Palouse soil amended with casamino acids, the inhibition seemed to increase with increasing relative humidity. The higher HC aerosol mass concentration in the test of higher relative humidity (see Table 2.5) might explain the dose effect of HC in the soil dehydrogenase activity.

TABLE 3.48. THE EFFECT OF RFT HC SMOKE EXPOSURES (HC-4, 5, 6, 7) ON SOIL DEHYDROGENASE ACTIVITY

	Dehydrogenase Activity (% of control [a])			
Exposure Time (h)	Burbank Soil		Palouse Soil	
	Glucose -Amended	Casamino Acids -Amended	Glucose -Amended	Casamino-Acids -Amended
1	128.25(9.90)*[b]	143.94(9.74)*	116.07(8.29)*	123.72(7.80)*
2	75.36(1.36)*	92.46(7.32)	100.00(5.62)	91.26(2.16)*
3	50.52(10.09)*	56.30(7.48)*	101.15(4.49)	107.49(10.59)
4	26.88(1.41)*	41.45(2.32)*	112.63(6.62)*	87.52(2.16)*

(a) Mean(±s. d.), n=3.
(b) *Denotes significant difference from control based on Student's t-test, $P \leq 0.05$

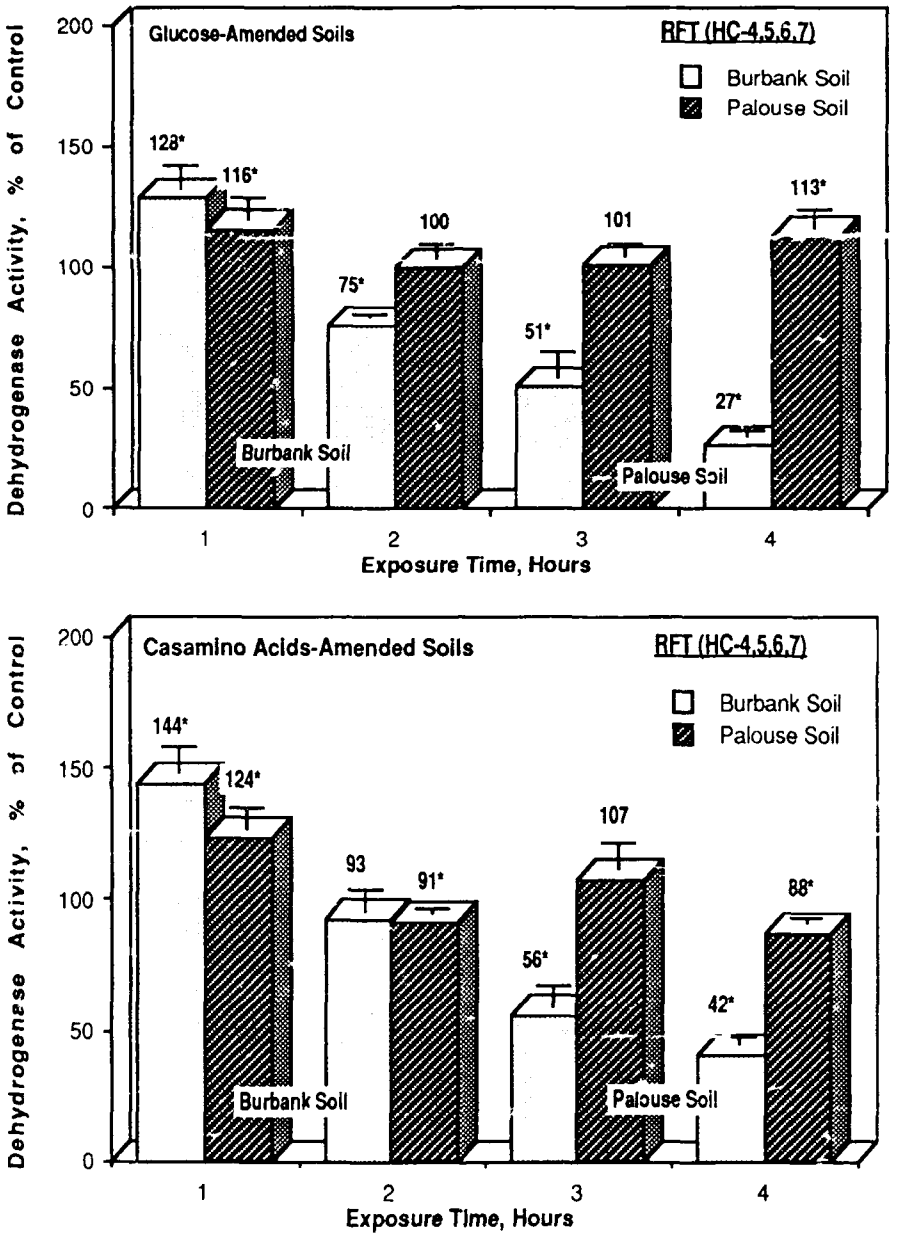


FIGURE 3.38. DEHYDROGENASE ACTIVITY (EXPRESSED AS % OF CONTROL) IN SOIL EXPOSED TO RFT HC SMOKE EXPOSURES. ERROR BARS REPRESENT STANDARD DEVIATIONS, N=3. *DENOTES SIGNIFICANT DIFFERENCE FROM CONTROL BASED ON t-TEST, $P \leq 0.05$

TABLE 3.49. THE EFFECT OF HC ON SOIL DEHYDROGENASE ACTIVITY BASED ON RELATIVE HUMIDITY

		Dehydrogenase Activity (% of control [a])			
		Burbank Soil		Palouse Soil	
RH (%)	Post-Exposure Time (weeks)	Glucose -Amended	Casamino Acids -Amended	Glucose -Amended	Casamino Acids -Amended
20	0	46.45(6.19)*[b]	37.92(3.94)*	62.29(4.05)*	86.73(2.86)*
	1.5	51.67(4.99)*	54.81(1.77)*	169.18(18.79)*	77.97(7.02)*
55	0	20.04(2.87)*	38.80(5.35)*	90.32(10.01)	68.26(1.65)*
	1	32.36(3.63)*	36.00(4.63)*	141.48(6.12)*	53.75(5.83)*
85	0	38.45(3.76)*	45.90(7.07)*	95.83(5.53)*	46.95(3.51)*
	2	29.67(1.62)*	26.01(1.75)*	125.16(3.29)*	51.00(2.34)*

(a) Mean(±s. d.), n=3.
(b) *Denotes significant difference from control based on Student's t-test, $P \leq 0.05$.

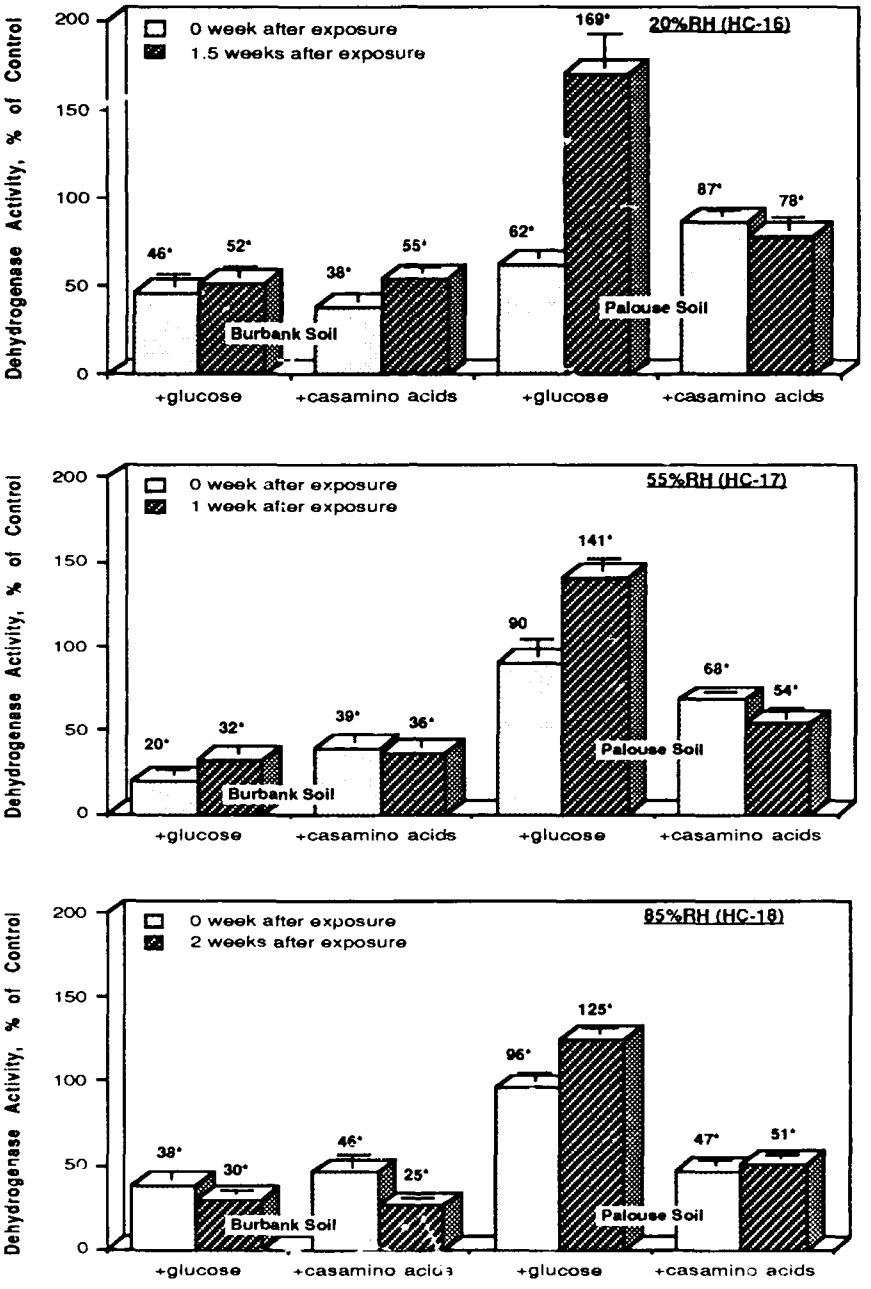


FIGURE 3.39. EFFECT OF HC SMOKE EXPO[illegible]E ON SOIL DEHYDROGENASE ACTIVITY BASED ON RE[illegible] HUMIDITY, EXPRESSED AS % OF CONTROL. ERROR BARS REPRESENT STANDARD DEVIATIONS, N=3. *DENOTES SIGNIFICANT DIFFERENCE FROM CONTROL BASED ON t-TEST, $P \leq 0.05$

In the cumulative dose of HC exposure, dehydrogenase activity in both Palouse and Burbank soil was severely inhibited (Table 3.50 and Figure 3.40). Although the degree of inhibition was greater in Burbank soil, the effect on Palouse soil was also severe. More than 80% of dehydrogenase activity was absent after cumulative HC exposure on soils amended with either glucose or casamino acids. A slight recovery of activity was observed in Palouse but not in Burbank soil 4 weeks after the last exposure.

TABLE 3.50. THE EFFECT OF CUMULATIVE HC EXPOSURES ON SOIL DEHYDROGENASE ACTIVITY

Post Exposure (Weeks)	Dehydrogenase Activity (% of control [a])			
	Burbank Soil		Palouse Soil	
	Glucose -Amended	Casamino Acids -Amended	Glucose -Amended	Casamino Acids -Amended
0	2.15(0.19)* [b]	1.93(0.14)*	8.19(0.42)*	10.65(1.01)*
1	1.57(0.07)*	1.53(0.44)*	4.82(0.17)*	5.60(0.40)*
2	3.54(0.29)*	3.32(0.48)*	5.91(0.60)*	6.15(0.85)*
4	1.34(0.52)*	1.18(0.17)*	6.71(0.34)*	15.07(1.23)*

(a) Mean(±s. d.), n=3.
(b) *Denotes significant difference from control based on Student's t-test, $P \leq 0.05$.

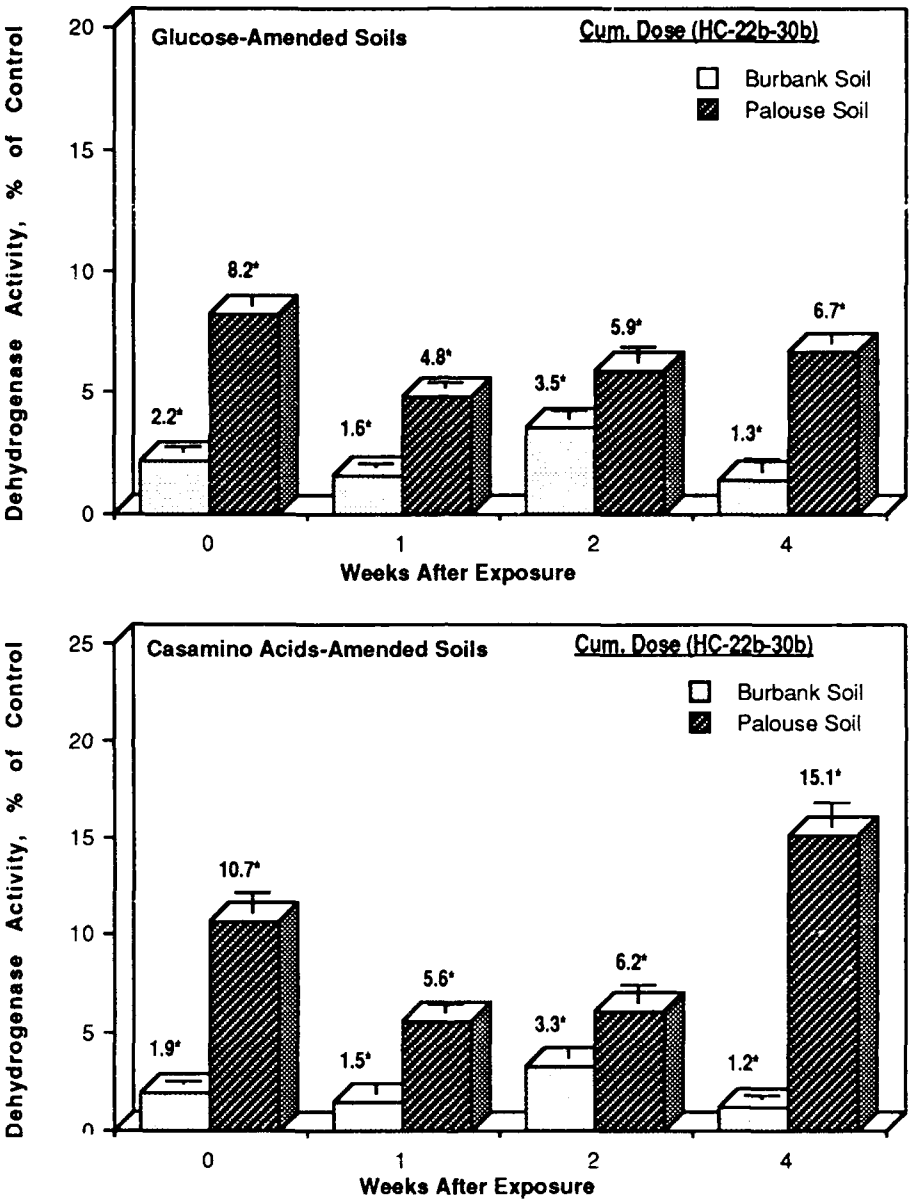


FIGURE 3.40. DEHYDROGENASE ACTIVITY (EXPRESSED AS % OF CONTROL) IN SOIL EXPOSED TO CUMULATIVE DOSES OF HC SMOKE EXPOSURES. ERROR BARS REPRESENT DIFFERENCE FROM CONTROL BASED ON t-TEST, $P \leq 0.05$

Soil Phosphatase Activity. Phosphatases, which can exist extracellularly, are a broad group of enzymes that cleave esters and anhydrides of phosphates from complex organophosphates and are important in the mineralization of phosphorus from soil organic matter (Ramirez-Martinez 1968). The phosphatase assay was not performed for the range-finding and relative humidity test series, hence no data are available regarding their effects. The effect of cumulative HC exposures on soil phosphatase activity is presented in Table 3.51 and illustrated in Figure 3.41. The effects were dependent on both soil type and incubation time. A reduction of more than 50% was observed for the Burbank soil; the inhibition increased upon incubation although some evidence of recovery was observed after 4 weeks. The activity in the Palouse soil was not reduced below the control when assayed immediately after the last exposure. However, the phosphatase activity decreased with prolonged incubation and was 50% of the control after 4 weeks.

TABLE 3.51. THE EFFECT OF CUMULATIVE HC EXPOSURE ON PHOSPHATASE ACTIVITY IN BURBANK AND PALOUSE SOILS

	Phosphatase Activity (% of control [a])	
Post Exposure (weeks)	Burbank Soil	Palouse Soil
0	45.50(1.58)* [b]	100.63(9.89)
1	37.57(4.06)*	96.49(2.69)
2	11.98(1.63)*	88.11(15.77)
4	30.23(1.72)*	51.10(4.88)*

(a) Mean(± S.D.), n=3.
(b) *Denotes significant difference from control based on Student's t-test, $P \leq 0.05$.

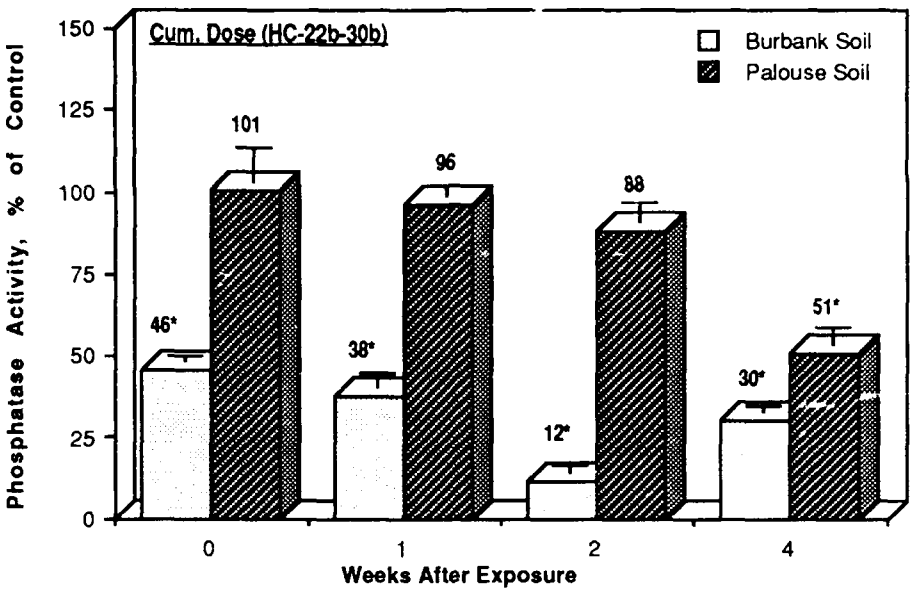


FIGURE 3.41. PHOSPHATASE ACTIVITY (EXPRESSED AS % OF CONTROL) IN SOIL EXPOSED TO CUMULATIVE DOSES OF HC SMOKE. ERROR BARS REPRESENT STANDARD DEVIATIONS, N=3. *DENOTES SIGNIFICANT DIFFERENCE FROM CONTROL BASED ON t-TEST, $P \leq 0.05$

Soil Nitrification. The conversion of soil organic nitrogen to available inorganic forms is accomplished by autotrophic bacteria. *Nitrosomonas* spp. and *nitrobacter* spp. are considered to be the most important bacteria mediating these conversion processes. This two species of autotrophs are generally regarded as being sensitive to environmetal toxicants. Assaying of the nitrifying bacteria in smoke-exposed soil is integral in the assessment of HC effect on soil microorganisms.

In Burbank soil, populations of *Nitrosomonas* are not significantly affected by smoke exposure of up to 4 h but *Nitrobacter* was not detected in soil exposed for 1h or more. In Palouse soil, *Nitrobacter* was eliminated after a 3-h exposure while *Nitrosomonas* was not significantly affected by HC smoke exposure (Table 3.52, as shown in Figure 3.42).

TABLE 3.52. THE EFFECT OF RFT HC EXPOSURES ON SOIL NITRIFIER POPULATIONS

Exposure Time (hours)	Log (MPN nitrifier population/g dry soil)[a]							
	Burbank Soil				Palouse Soil			
	Nitrosomonas		*Nitrobacter*		*Nitrosomonas*		*Nitrobacter*	
	C[b]	E[c]	C	E	C	E	C	E
0	3.23	3.52	1.30	<1	3.38	1.30	1.65	1.89
1	3.23	2.34	1.30	<1	3.38	2.34	1.65	1.65
2	3.23	3.23	1.30	<1	3.38	2.90	1.65	<1
4	3.23	3.04	1.30	<1	3.38	1.89	1.65	<1

(a) 95% confidence interval for these MPN data = ± 0.52.
(b) Control soil, soil not exposed to HC smoke.
(c) Exposed soil, soil exposed to cumulative dose HC smoke.

The effect of HC on soil-nitrifying bacteria based on relative humidity is presented in Table 3.53 and illustrated in Figure 3.43. *Nitrosomonas* in both soils was only slightly affected by the HC aerosol of 20 to 85% relative humidity, but *Nitrobacter* was about one magnitude lower than the unexposed control.

TABLE 3.53. THE EFFECT OF HC RELATIVE HUMIDITY ON SOIL-NITRIFYING BACTERIA IMMEDIATELY FOLLOWING EXPOSURE

Exposure (RH)	Log (MPN Nitrifier Population/g Dry Soil)[a]			
	Burbank Soil		Palouse Soil	
	Nitrosomonas	*Nitrobacter*	*Nitrosomonas*	*Nitrobacter*
C[b]	2.85	1.43	3.38	1.69
20%	2.52	0.30	2.34	0.83
55%	2.69	0.30	2.43	0.60
85%	2.52	0.30	2.69	0.83

(a) 95% confidence interval for these MPN data = ± 0.52.
(b) Control soil, soil not exposed to HC smoke.

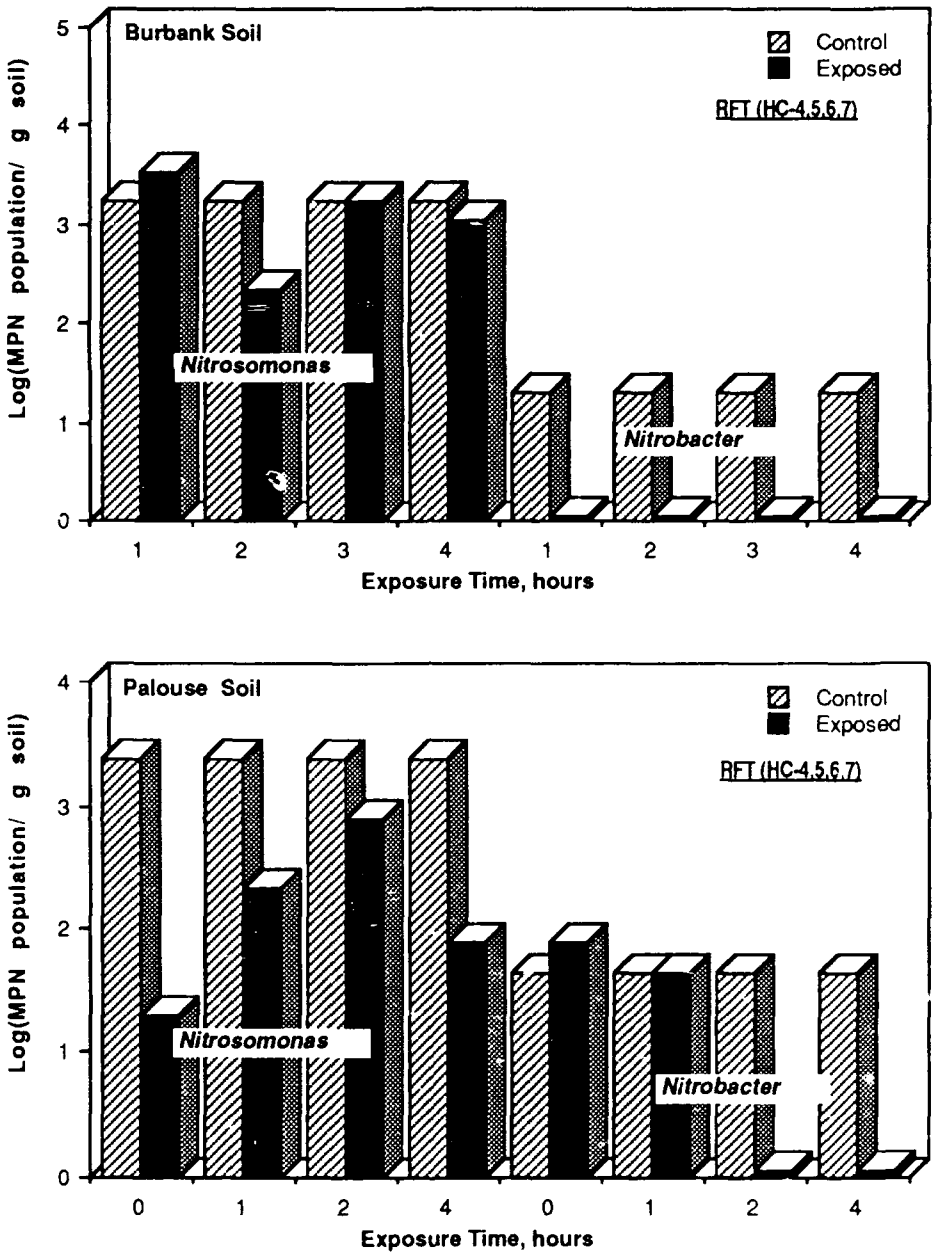


FIGURE 3.42. EFFECT OF RFT HC EXPOSURES ON SOIL NITRIFIER POPULATIONS. 95% CONFIDENCE INTERVAL FOR THESE MPN DATA IS ± 0.52

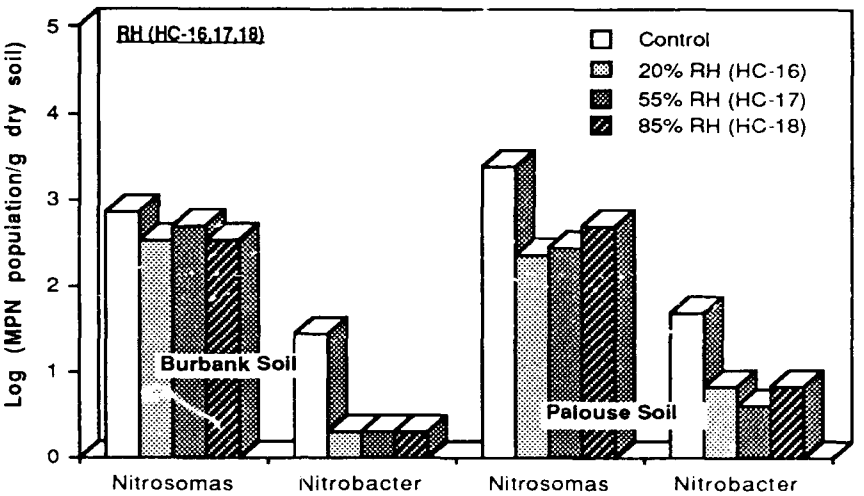


FIGURE 3.43. THE EFFECT OF HC RELATIVE HUMIDITY ON SOIL-NITRIFYING BACTERIA IMMEDIATELY FOLLOWING EXPOSURE. 95% CONFIDENCE INTERVAL FOR THESE MPN DATA IS $\pm$ 0.52

Soil-nitrifying bacteria were affected by the exposure to the cumulative dose of HC as shown in Table 3.54 and Figure 3.44. Both nitrifying bacteria, *Nitrosomonas* spp. and *Nitrobacter* spp., were reduced below the detection limit in Burbank soil. *Nitrosomonas* populations in Palouse soil were ~70% of the control immediately after the last exposure and declined to ~25% 4 weeks later. *Nitrobacter* in Palouse soil diminished to below the detection limit immediately and did not recover.

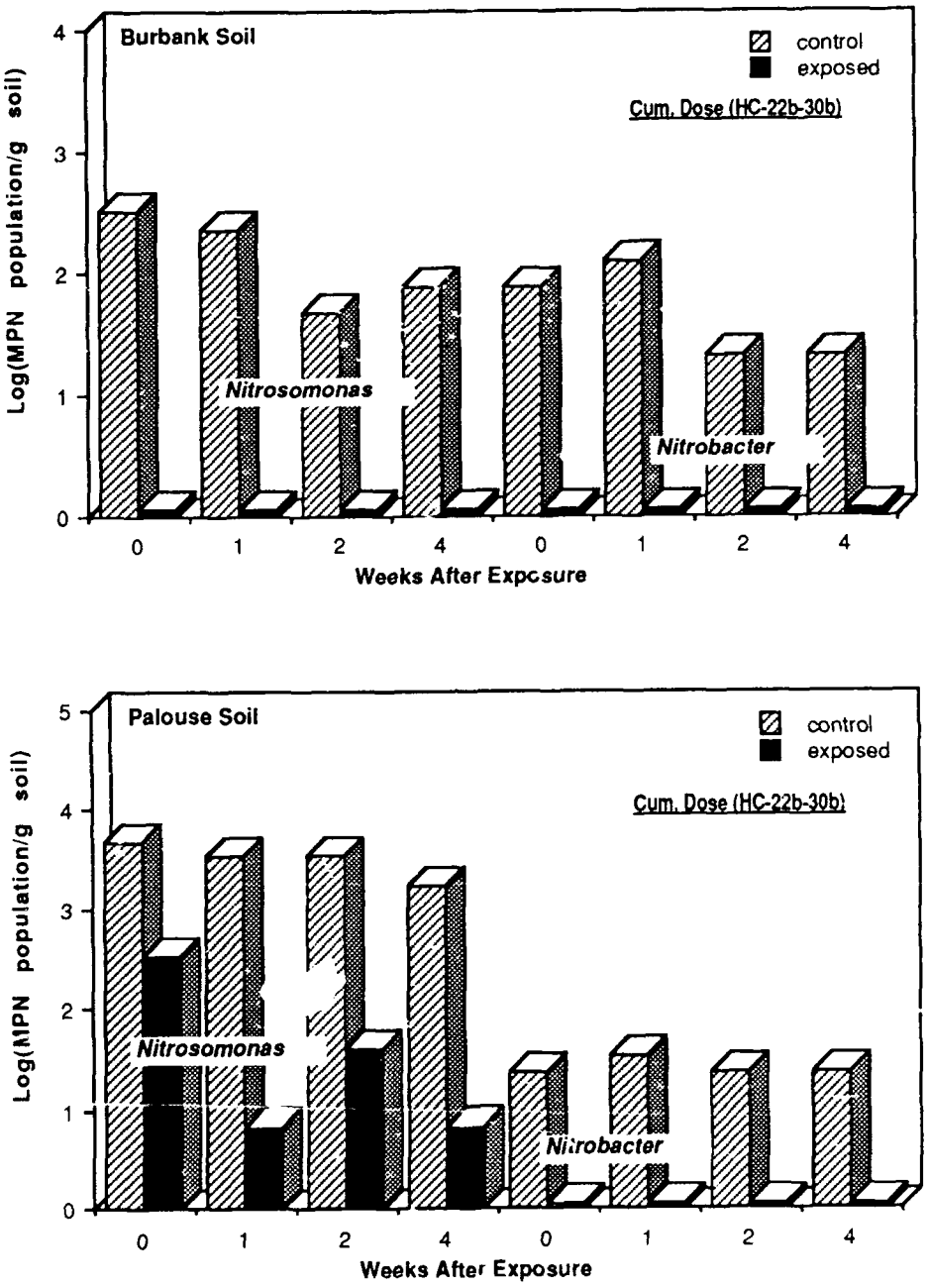


FIGURE 3.44. THE EFFECT OF CUMULATIVE DOSES OF HC EXPOSURE ON SOIL NITRIFYING BACTERIA IMMEDIATELY FOLLOWING EXPOSURE. 95% CONFIDENCE INTERVAL FOR THESE MPN DATA IS $\pm$ 0.52

TABLE 3.54. THE EFFECT OF CUMULATIVE HC EXPOSURES ON SOIL NITRIFIER POPULATIONS

	Log (MPN Nitrifier Population/g Dry Soil)[a]							
Post Exposure (weeks)	Burbank Soil				Palouse Soil			
	Nitrosomonas		*Nitrobacter*		*Nitrosomonas*		*Nitrobacter*	
	C[b]	E[c]	C	E	C	E	C	E
0	2.52	<1	1.90	<1	3.66	2.52	1.36	<1
1	2.36	<1	2.11	<1	3.52	0.83	1.52	<1
2	1.69	<1	1.34	<1	3.52	1.60	1.36	<1
4	1.90	<1	1.34	<1	3.23	0.83	1.36	<1

(a) 95% confidence interval for these MPN data = ± 0.52.
(b) Control soil, soil not exposed to HC smoke.
(c) Exposed Soil, soil exposed to cumulative dose HC smoke.

3.8 SOIL INVERTEBRATE EFFECTS

The standard earthworm bioassay using a defined synthetic soil was performed for the WST series. This involves exposure of three replicate plates containing five worms each. These were exposed to HC aerosols at 2, 4, 6, and 10 mph for 2 h. Mass loading to each plate and treatment were determined; the dose was calculated at 0.87±0.25, 2.31±1.42, 3.72±2.36, and 8.21±1.93 μg Zn/cm^2 for the 2- to -10 mph treatments, respectively. Survival after 2 weeks was 100% for all treatments, including controls. It is assumed that at these relatively low dose rates, neither the Zn or organic constituents of HC smokes are toxic to earthworms.

4.0 SUMMARY AND CONCLUSIONS

Hexachloroethane (HC) smokes were generated and delivered using an environmentally controlled recirculating wind tunnel. Several study scenarios were performed. These included: 1) a Range-Finding test to assess the environmental impact of dose and exposure time; 2) a Relative Humidity test to assess the effects of relative humidity on aerosol aerodynamics, chemistry, and deposition processes; 3) a Wind Speed test to assess the changes in surface deposition and biotic effects resulting from changes in wind speed between 2 and 10 mph; and 4) a Cumulative Dose test that evaluated the biotic impacts from repetitive exposure to smokes. In addition, the behavior of HC aerosols was based on aerodynamic characteristics for each environmental variable and test series. Deposition efficiency was calculated based on deposition velocities. Environmental impacts were based on mass loading/dose to either foliar surfaces or soil systems.

Air concentrations of HC smoke were maintained at approximately 500 mg/m^3 for all test series except for the Cumulative Dose tests, which were established at 150 and 700 mg/m^3 for the low- and high-dose scenarios, respectively. The MMAD (±GSD) for the aerosols averaged 1.7 µm (1.5) for all test series, with relative humidity having a direct effect on MMAD; MMAD values increase from 1.7 to 2.1 µm as relative humidity is increased from 20 to 85%. This has a pronounced influence on deposition to foliar and soil surfaces. Moisture content varied with humidity and other test conditions.

HC smokes contain >50% extractable $ZnCl_2$ on a mass basis, with chlorocarbon compounds comprising slightly >1% of the mass; the remainder of the mass is associated with insoluble carbonaceous ash. The results indicate that most, if not all, of the biotic effects can be assigned to either Zn or acidity of HC smoke. The chlorocarbon compounds, including CCl_4, C_2Cl_4, C_2Cl_6, and C_6Cl_6, are found to be in concentrations of 5 to 7 mg/m^3. The environmental half-life of organics associated with plant foliage ranged from 1 to 80 days, and was dependent on both plant type and relative humidity. Half-lives for soils were higher than for plant surfaces, and ranged from 5 to 70 days. No phosgene was detected.

Results of HC deposition studies for soils and deposition plates indicate that acidification of the soils to levels comparable to those of the wet deposition plates generally causes similar solubilization characteristics as those found on exposed soils. As expected, delaying water contact had no observed effect; this is in contrast to the significant effect on P speciation resulting from phosphorous aerosols reported earlier (Van Voris et al. 1987). Chloride concentrations must be used for determination of deposition velocities to soils, because of the wide range of mineralization rates and the inefficiency of weak acid leachates in removing deposited Zn from the different soils. Depression of nitrate in some exposed soils

likely reflects the initial suppression of microbial activity. No lasting deleterious effects are anticipated for soils receiving smoke doses comparable to those simulated in the present studies. In these studies, thin soil lenses were employed to maximize effects. The much deeper natural soil profiles and intermittent precipitation events should readily reduce soil and biotic impacts resulting from Zn, Al, and acidity associated with HC smoke usage.

As had been observed with the previous smokes (Van Voris et al. 1987; Cataldo et al. 1988), mass loading of the tissues increased with both exposure time and increasing wind speed. Overall, phytotoxicity from HC smokes is minimal, slightly greater than observed for fog oil smokes (Cataldo et al. 1988), but substantially less than for the phosphorus smokes (Van Voris et al. 1987). There appeared to be a significant effect of increased relative humidity on foliar mass loading at 55 and 85% RH, compared to 20% RH, at least for some plant species. Postexposure leaching significantly reduced the original mass loading levels with a concomitant reduction in phytotoxic effects. The pines and sagebrush exhibited slightly higher mass loading rates, which may be related to foliar morphology. The overall phytotoxicity of the HC smokes to vegetation appeared to be linked either to the degree of Zn deposition (accumulation) to the tissues during the course of the exposures, or to the acidity of the smokes. Under all exposure conditions, the bush bean proved to be the most sensitive in exhibiting both visual and physiological (photosynthesis/respiration) phytotoxic responses, with the ponderosa pine appearing to be the least sensitive of those species tested. Although dry matter accumulation in the grasses was reduced immediately following exposure, regrowth rates for subsequent harvests of foliarly exposed plants did not significantly differ from those of the controls. Secondary effects on dry matter accumulation by grasses grown in exposed soils were not evident following any of the exposures. While a significantly elevated tissue concentration of Zn was present in these plants, there were no apparent interactions of Zn or Al on the mineral nutrition of exposed plants.

Soil subjected to HC exposure did exhibit inhibition of soil respiration, and of dehydrogenase and phosphatase activities, and a decline in populations of nitrifying bacteria. The inhibition depends largely on soil types as well as HC aerosol mass concentration. Exposures for 1 or 2 h under the test conditions exhibit no effect on soil dehydrogenase activity, but prolonged exposure for up to 4 h does inhibit soil respiration and enzymatic activities. Inhibition of nitrifying bacteria is less pronounced in Palouse soil than in Burbank soil, and *Nitrosomonas* spp. was less sensitive to HC smoke exposure than *Nitrobacter* spp. Reduced soil respiration and dehydrogenase activity was also observed in soils subject to HC aerosol under various relative humidities. The only exception is for Palouse soil amended with glucose, which showed enhanced dehydrogenase activity at 1 to 2 weeks of postexposure time. Again the results indicate that *Nitrosomonas* spp. was less sensitive to HC smoke exposure than *Nitrobacter* spp. When soils were repeatedly exposed to HC aerosol smoke,

the soil respiration was inhibited and enzymatic activities were dramatically reduced. Soil dehydrogenase decreased to 1-15% of unexposed control in both soil types tested. Phosphatase declined to 12-51% of unexposed control in Burbank soil while some effect was apparent after 4 weeks. The cumulative dose tests also showed that *Nitrosomonas* spp. was less sensitive to exposure than *Nitrobacter* spp. in Palouse soil; however, both groups of nitrifiers were reduced to below detection limit in Burbank soil. Results indicate that HC aerosol smoke may likely to have a negative impact on soil microbial activities and populations, but only under recurrent use. Earthworm survival was not impacted by HC aerosols deposited to soils at dose rates of 8 μg Zn/cm^2 or 32 μg HC/cm^2.

Overall, HC smokes are less toxic to terrestrial biota than were the phosphorus smokes (Van Voris et al. 1987), but HC smokes are more toxic than was observed for the fog oil smokes (Cataldo et al. 1988). The biotic effects noted appear to be based on increased Zn loads to soils or vegetation, or may be based on transient changes in soil or foliar pH resulting from the acidity of HC aerosols.

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